Effect of superplasticizer on the performance properties of cemented paste backfill at different curing temperatures

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Abstract

Cemented paste backfill (CPB) technology is widely used in the mining industry as an effective means of tailings disposal. CPB is a mixture of tailings, binder, water, and additional admixtures when required. It is prepared in a mixing plant on the ground surface and then transported into the mine cavities through pipelines either by gravity and/or using pumps. To ensure efficiency during transportation and avoid pipe clogging (which can cause unnecessary delays and loss of productivity), fresh CPB must have sufficient flowability. To achieve that, high-range water reducing admixtures, also known as superplasticizers, are usually added to the CPB during mixing. These admixtures are widely used in the construction industry due to their ability to improve flowability without undermining other important engineering properties. However, their influence on the rheology, mechanical strength and environmental performance (reactivity and permeability) of CPB is not fully understood. Thus, experimental studies were conducted to investigate the effects of superplasticizers on the performance properties of cemented paste backfill at different curing temperatures.

Yield stress and viscosity of fresh CPB cured for 0, 1, 2, and 4 hours were measured using a vane shear device and a Brookfield Viscometer respectively. Unconfined compressive strength (UCS) of samples cured for 1, 3, 7, and 28 days was determined in accordance with ASTM – C39. Superplasticizer contents were varied as 0%, 0.125%, and 0.25% of the total weight of the CPB. Preparations and curing of the specimens were performed at controlled conditions of 2, 20, and 35 ºC to investigate the effect of ambient or curing temperatures. To have a better understanding of the environmental performance of CPB containing superplasticizer, reactivity, and hydraulic conductivity up to 90 days of curing were also investigated. The reactivity was measured using oxygen consumption test while hydraulic conductivity was measured using flexible wall permeability test. Microstructural analyses (thermogravimetric analyses, X-Ray diffraction, and mercury intrusion porosimetry) and monitoring tests (pH, zeta potential, electrical conductivity, and matric suction) were carried out to understand the principles behind the changes of the observed properties. The obtained results show that superplasticizer dosage and temperature variation have significant effects on the rheology, strength development, hydraulic conductivity and reactivity of the CPB. The polycarboxylic ether-based superplasticizer significantly reduces the yield stress and viscosity by creating strong electrostatic repulsion between the solid particles in the CPB and by steric hinderance. The CPB containing the superplasticizer remains fluid for longer period (as compared with the CPB without superplasticizer) due to the retardation of binder hydration. However, high curing temperature induces faster cement hydration, which thickens the fresh CPB. The unconfined compressive strength (UCS) of the CPB containing superplasticizer was observed to be lower in the early age (up to 7 days), which is also attributed to retardation of the binder hydration. At later ages, the superplasticizer improves the mechanical strength as the binder hydration accelerates and the solid particles self-consolidate. Coupled THMC processes in the CPB showed the role played by the changes in electrical conductivity, volumetric water content, matric suction, and temperature on the development of mechanical strength of the CPB containing superplasticizer. Similarly, addition of the superplasticizer in the CPB decreases both the hydraulic conductivity and reactivity of CPB, thus improving its environmental performance. The improvement is largely attributed to enhanced binder hydration and self-consolidation which decrease the porosity of the CPB. Increasing the curing temperature was found to magnify the improvement of the CPB properties by inducing faster binder hydration. The findings from this study will undoubtedly inform the design of CPB structure with better mechanical stability and environmental performance.

Dedication

To my late dad, may his soul continue to rest in peace.

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Chapter 1. Introduction

1.1. Background

Large amount of waste is generated from the mining operations in the form of tailings whose disposal has been of great concern to the industry for many years. Tailings is a general term used for the slurry of finely crushed rock and water produced after the extraction vital minerals at the mines. They are usually toxic if exposed to the environment to a degree depending on the traces of elements they contain (Ma et al., 2002; Benzaazoua et al., 2004). If fact, tailings are considered to be the single most important mining byproduct with significant environmental impact (Fall and Benzaazoua, 2003; Reid et al., 2009). A proper and safe disposal mechanism has become an important regulatory demand for mining projects to be approved (Vick, 1984).

Backfilling is important because the footprint left behind after underground mines are exhausted poses danger to the safety of human lives, animal, and the environment. It has, therefore, become a common tradition in the mining industry all over the world to refill the shafts and tunnels that necessitated the mining process. However, it must be understood that backfills are essentially employed in the strengthening of underground mines as the mining process goes deeper into the ground. Backfilling during mining ensures that proper support is provided to the exposed pillars so that excavation can proceed without high risks of collapse (Donovan, 1999; Benzaazoua et al., 2004; Belem et al., 2006; Jiang et al. 2019). Also, the backfills are employed to control the buckling or caving in of the mines as a result of the accumulation of weights on top of the mines (Zhang et al., 2015).

One of the widely used backfill technology with considerable efficiency in mine waste management is cemented paste backfill (CPB). CPB is a mixture of milled tailings, hydraulic binder, water and additional additives when required (Wu et al., 2015; Ercikdi et al., 2009; Fang and Fall, 2020). It provides a safer means of disposing the tailings as compared to surface disposal that is associated with environmental contamination and risk of dam failures (Azam and Li, 2010; Aldhafeeri et al., 2016). Furthermore, CPB is an effective means of providing ground support (important for the safety of the miners) and reduces the mining cycle, which increases the overall productivity of the mining operations (Yin et al., 2012; Li, 2014; Cui and Fall, 2017a, 2017b). A schematic overview of the CPB technology is shown in Figure 1.1. Typically, the constituents of the CPB are mixed together on the ground surface and then transported into the mine cavities by gravity, with a pump or using the combination of the two. For this to be achieved effectively, the fresh CPB needs to have an appropriate flowability that will allow it to be transported without clogging the pipe system (Wu et al., 2013; Ercikdi et al., 2017). A practical and efficient solution is to add a high range water reducing admixtures, also known as superplasticizers, in the fresh CPB mix. Unlike other construction materials such as concrete, the effects of the superplasticizers on the engineering performance or properties (e.g., rheological, mechanical, and environmental) of CPB has not been fully studied.

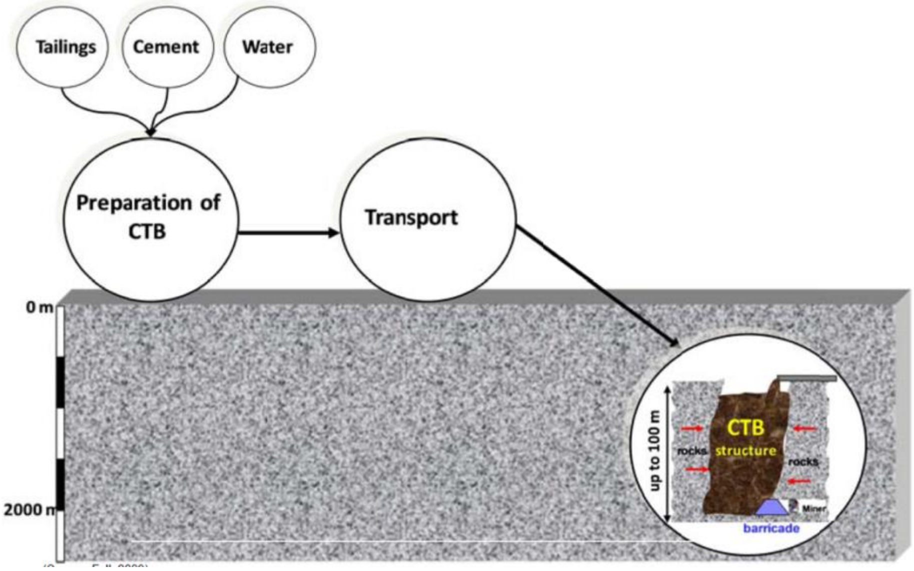


Figure 1.1. Schematic representation of CPB Technology (Fall et al., 2008)

Primarily, the main purpose of the superplasticizers is to improve the rheology of a fresh contentious material to allow easy mixing, transportation, and placement. However, they can affect structures in different ways based on the manner in which they interact with the binder and the other constituents in the mixture (Griesser, 2002; Jansen et al., 2012; Pan et al., 2016). This has a tendency of influencing both early age and long-term strength properties as observed from many studies on concrete (Periera et al., 2012; Alsadey, 2015; Bravo et al., 2017). The chemical interaction can extend to the natural reaction within tailings materials used in CPB under varying environmental conditions (mainly sulphate reaction that generates acid mine drainage- AMD) (Wu et al., 2020). Thus, the amount of toxic chemicals produced and how they may be leached from the CPB could be influenced by the superplasticizers. Therefore, studying the effects of superplasticizers on both geotechnical and environmental performance of CPB is important to ensure proper and sustainable backfill design.

1.2. Problem statement

Efficiency in the transportability of fresh CPB from the mixing plant on the ground surface to underground stopes is largely dependent on its fluidity or flowability. A fresh CPB with poor flowability may cause pipe clogging during transportation, resulting in the shutdown of the system, and ultimately causing unnecessary delay. With the backfilling process constituting about 20% of the total mine operation cost (Fall et al., 2008), any delay can have a huge financial implication on the mining process. To improve the transportability, high range water reducing admixtures, also known as superplasticizers, are often used in the preparation of the CPB. These materials have the ability of reducing the mixing water by 12 – 30% while maintaining its desirable workability and consistency (Barabanschikov and Komarinskiy, 2014). However, as for any admixture used in a cementitious material, it is important to understand both short- and long-term effects on other engineering properties of CPB material containing superplasticizers.

The literature on the use of superplasticizers in the CPB is limited to the rheological and mechanical behaviour without considering effects on other important parameters such as temperature, reactivity, and permeability. The available published research on rheology of CPB considered factors such as superplasticizer dosage (Mangane et al., 2018; Ouattara et al., 2017; Ouattara et al., 2018; Panchal et al., 2018; Yang et al., 2018; Guo et al., 2021) and superplasticizer type (Simon and Grabinsky, 2011; Ouattara et al., 2017; Guo et al., 2021). None of the studies considered the influence of temperature on the rheology of CPB containing superplasticizer, despite it being a crucial factor on the CPB performance (Fall and Samb, 2009; Pokharel and Fall, 2013; Wu et al., 2014; Aldhafeeri et al. 2016). Temperature can vary significantly from subzero in some regions to over 40 ^{o}C in other regions due to weather and climate variabilities (Wu et al., 2012; Alakangas et al., 2013). Also, heat can be introduced to the CPB from the exothermal reaction of the binder or from the deep geothermal source (Oreharena and Fall, 2008; Mozaffaridana, 2011; Huan et al., 2021). Another important factor essential for a proper design of CPB structures is the reactivity due to the tendency of superplasticizer to interact with other chemical components (Prince et al., 2002; Mollah et al., 2000). Some recent studies have established the occurrence of AMD in CPB made from sulphide-bearing tailings (e.g., Ouellet et al., 2003; Ouellet et al., 2006; Benzaazoua et al., 2008; Aldhafeeri and Fall 2016, 2017), but no research has been conducted on the reactivity of CPB containing superplasticizers. The seepage or leaching of the generated environmentally toxic chemical compounds from AMD into surface or groundwater bodies is also vital towards a sustainable design of CPB structures. For this reason, the hydraulic conductivity is used as a measure for environmental performance of CPB. There is currently no research study on the hydraulic conductivity of CPB containing superplasticizers. Therefore, this PhD research will experimentally investigate the effects of superplasticizer on these unexplored performance properties of CPB.

1.3. Research objectives

The main goal of the PhD research is to provide a compressive insight into the effects of superplasticizers on the performance properties of cemented paste backfill at different curing temperatures. The specific objectives are:

- To investigate the effects of polycarboxylate ether-based superplasticizer on the rheological properties of CPB with emphasis on yield stress and viscosity.
- To study effects of a polycarboxylate ether-based superplasticizer on the evolution of heat of hydration in CPB systems.
- To study effects of a polycarboxylate ether-based superplasticizer on the saturated hydraulic conductivity of CPB.
- To study effects of a polycarboxylate ether-based superplasticizer on the reactivity of CPB.
- To investigate the influence of curing temperature on the rheology, hydraulic conductivity, and reactivity of CPB.
- To investigate the influence of initial sulphate content on the rheology, hydraulic conductivity, and reactivity of CPB.

1.4. Research approach and methods

The objectives of this research study are attempted to be addressed using laboratory experiments. A flow chart outlining the research method is shown in Figure 1.2.

Preliminary review of the literature and a study of the theoretical background on the subject facilitated the election of appropriate test methods for the investigations. CPB mixtures were prepared using both natural tailings and non-reactive artificial silica tailings. The use of synthetic tailings allows for a proper control of the variables so that behaviours can easily be associated with the most probable cause. Portland cement type I (PCI), fly ash (FA) and blast furnace slag (Slag) in different proportions were used as binders. A polycarboxylic-based superplasticizer with a commercial name of Master Glennium 7500 was used throughout the research as the water reducing admixture. Main geotechnical properties investigated were yield stress, viscosity, reactivity, hydraulic conductivity, and heat of binder hydration. Prepared CPB mixtures were prepared and cured under controlled temperature environments to simulate typical mining field settings.

Microstructural analyses and monitoring tests were employed to have a better understanding of the mechanisms responsible for the behaviors observed from various tests. Zeta potential, electrical conductivity, matric suction and pH monitoring were performed on fresh CPB in order to examine changes caused by binder hydration under the influence of the superplasticizer and curing temperatures. Mercury intrusion posorimetry (MIP), thermal analyses (TG/DTG), and X-ray diffraction (XRD) were conducted on some selected dried CPB samples. Detailed description of all the experimental tests conducted are presented in the respective chapters.

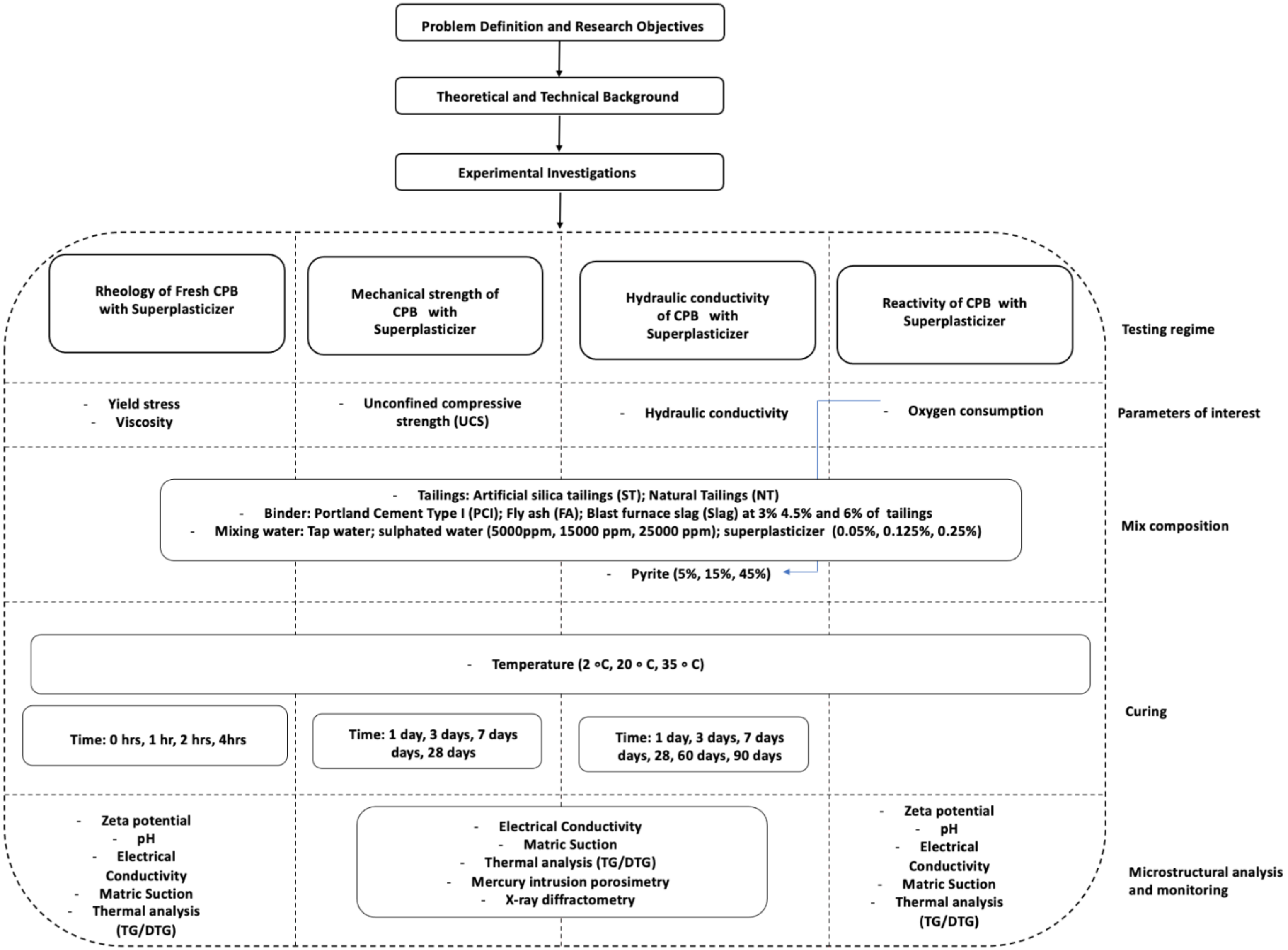


Figure 1.2. Research and study approach

1.5. Organization of the thesis

The PhD manuscript will be organized into nine chapters as presented in Figure 1.3. The tasks are discussed in an order that allows an effective achievement of the research objectives.

Chapter One provides a general background of the study including problem statements, research objectives, research approach and methods. **Chapter Two** presents a compressive technical background on the CPB technology, its types, properties, and factors that affect its mechanical and environmental properties. In addition, literature review on the use of superplasticizers in CPB was included to identify current research gaps. **Chapter Three** through **Six** are presented in technical paper format, with a total of four published articles. Each technical paper has an introduction; materials and methods; result and discussion; and well as summary and conclusion sections. It is important to mention that some information is repeated in the papers because they contain the main results of the PhD research are contained therein. Each paper was written independently in accordance with the instructions for manuscript submissions of the corresponding peer-reviewed journal. In **Chapter Seven**, the whole results obtained from the PhD research are synthesized with respect to the research objectives. Finally, the overall summary, conclusions, and recommendations for future research are contained in **Chapter Eight**.

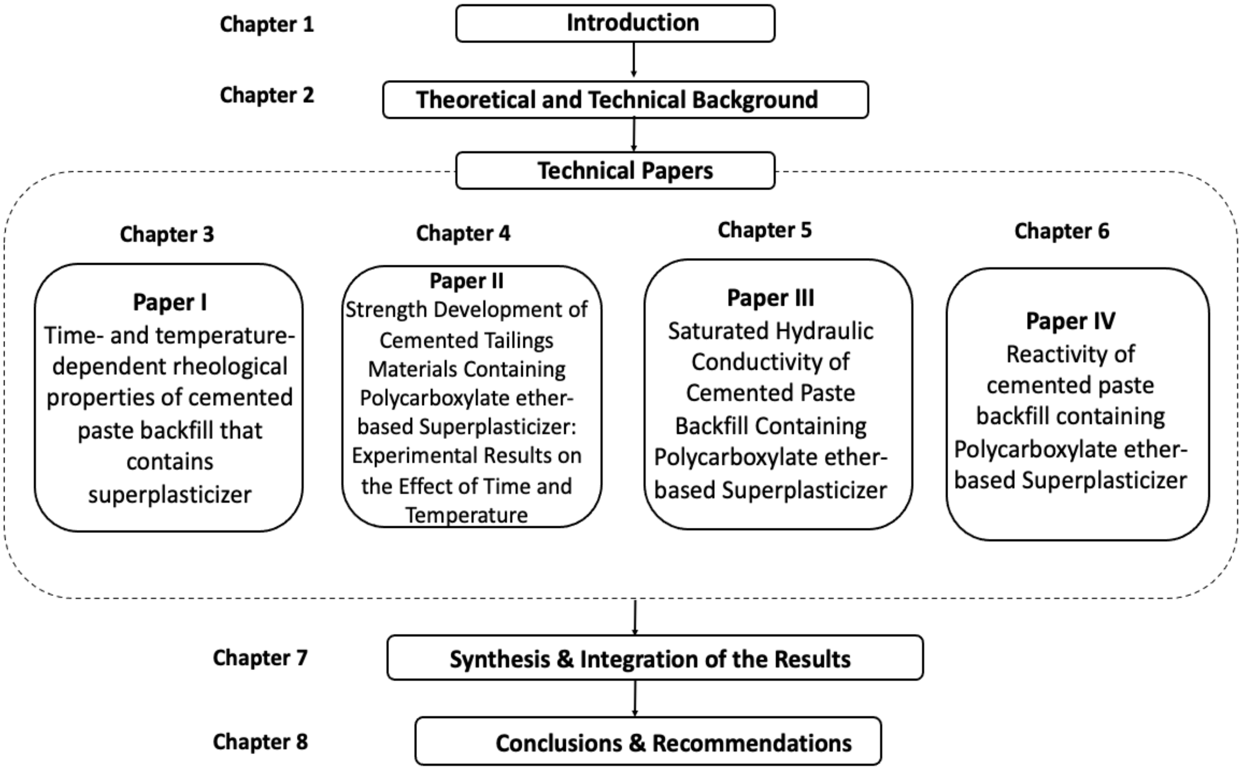


Figure 1.3. Thesis organization

1.6. References

Alakangas, L., Dagli, D., & Knutsson, S. (2013). Literature review on potential geochemical and geotechnical effects of adopting paste technology under cold climate conditions.

Aldhafeeri, A., & Fall, M., (2017). Sulphate induced changes in the reactivity of cemented tailings backfill. *International Journal of Mineral Processing 166* (10),13-23.

Aldhafeeri, Z., & Fall, M. (2016). Time and damage induced changes in the chemical reactivity of cemented paste backfill. *Journal of Environmental Chemical Engineering*, *4*(4), 4038-4049.

Aldhafeeri, Z., Fall, M., Pokharel, M., & Pouramini, Z. (2016). Temperature dependence of the reactivity of cemented paste backfill. *Applied geochemistry*, *72*, 10-19.

Alsadey, S. (2015). Effect of superplasticizer on fresh and hardened properties of concrete. *Journal of Agricultural Science and Engineering*, *1*(2), 70-74.

Azam, S., & Li, Q. (2010). Tailings dam failures: a review of the last one hundred years. *Geotechnical news*, *28*(4), 50-54.

Barabanshchikov, Y. G., & Komarinskiy, M. V. (2014). Influence of superplasticizer S-3 on the technological properties of concrete mixtures. Advanced Materials Research, 941.

Belem, T., Aatar, O. El., Bussière, B., Benzaazoua, M., Fall, M., & Yilmaz, E. (2006). Self-weight consolidation of column of cemented pastefill. 7th Seminar on paste and thickened tailings, April 2006, Irlande, 13p.

Benzaazoua, M., Perez, P., Belem, T., & Fall, M., (2004). A laboratory study of the behaviour of surface paste disposal. 8th International Symposia on Mining with Backfill. In Beijing, China, 2004. p. 181-192.

Benzaazoua, M., Marion, P., Picquet, I., & Bussière, B. (2004). The use of pastefill as a solidification and stabilization process for the control of acid mine drainage. *Minerals engineering*, *17*(2), 233-243.

Benzaazoua, M., Bussière, B., Demers, I., Aubertin, M., Fried, É., & Blier, A. (2008). Integrated mine tailings management by combining environmental desulphurization and cemented paste backfill: Application to mine Doyon, Quebec, Canada. *Minerals engineering*, *21*(4), 330-340.

Bois, D., Poirier, P., Benzaazoua, M., Bussière, B., & Kongolo, M. (2005). A feasibility study on the use of desulphurized tailings to control acid mine drainage. *Cim Bulletin*, *98*(1087), 74-74.

Cui, L., & Fall, M. (2017a). Multiphysics model for consolidation behaviour of cemented paste backfill. A*CSE International Journal of Geomechanics 17*(3), 04016077-23.

Cui, L, & Fall M. (2017b). Modeling of pressure on retaining structures for fill mass. *Tunnelling and Underground Space Technology 69*, 94-107.

Donovan, J. G. (1999). *The effects of backfilling on ground control and recovery in thin-seam coal mining* (Doctoral dissertation, Virginia Polytechnic Institute and State University).

Ercikdi, B., Cihangir, F., Kesimal, A., Deveci, H., & Alp, İ. (2009). Utilization of industrial waste products as pozzolanic material in cemented paste backfill of high sulphide mill tailings. *Journal of hazardous materials*, *168*(2-3), 848-856.

Ercikdi, B., Cihangir, F., Kesimal, A., & Deveci, H. (2017). Practical importance of tailings for cemented paste backfill. In *Paste tailings management* (pp. 7-32). Springer, Cham.

Fall, M., & Benzaazoua, M. (2003). Advances in predicting performance Properties and Cost of Paste Backfill. In Proceedings of International Conference of Tailings & Mine Waste '03, October 12-15, 2003, Colorado, USA. Ed. Balkema, pp.73-85.

Fall, M., Benzaazoua, M. and Saa, E.G., 2008. Mix proportioning of underground cemented tailings backfill. *Tunnelling and Underground space technology*, *23*(1), pp.80-90.

Fall, M., & Samb, S. S. (2009). Effect of high temperature on strength and microstructural properties of cemented paste backfill. *Fire Safety Journal*, *44*(4), 642-651.

Fang, K., & Fall, M. (2020). Shear Behavior of the Interface between Rock and Cemented Backfill: Effect of Curing Stress, Drainage Condition and Backfilling Rate. *Rock Mechanics and Rock Engineering, 53*:325-336.

Griesser, A. (2002). *Cement-superplasticizer interactions at ambient temperatures* (Doctoral dissertation, Swiss Federal Institute of Technology Zurich).

Guo, Z., Qiu, J., Jiang, H., Xing, J., Sun, X., & Ma, Z. (2021). Flowability of ultrafine-tailings cemented paste backfill incorporating superplasticizer: insight from water film thickness theory. *Powder Technology, 381*, 509-517.

Huan, C., Zhang, S., Zhao, X., Li, S., Zhang, B., Zhao, Y., & Tao, P. (2021). Thermal Performance of Cemented Paste Backfill Body Considering Its Slurry Sedimentary Characteristics in Underground Backfill Stopes. *Energies*, *14*(21), 7400.

Jansen, D., Neubauer, J., Goetz-Neunhoeffer, F., Haerzschel, R., & Hergeth, W. D. (2012). Change in reaction kinetics of a Portland cement caused by a superplasticizer—Calculation of heat flow curves from XRD data. *Cement and Concrete Research, 42*(2), 327-332.

Jiang, H. Fall, M., Li, Y., & Han, J. (2019). An experimental study on compressive behaviour of cemented rockfill. *Construction and Building Materials 213*,10-19.

Li, L. (2014). Generalized solution for mining backfill design. *International Journal of*

Geomechanics, *14*(3), 04014006.

Ma, Y., Dickinson, N., & Wong, M. (2002). Toxicity of Pb/Zn mine tailings to the earthworm Pheretima and the effects of burrowing on metal availability. *Biology and Fertility of Soils*, *36*(1), 79-86.

Mangane, M. B. C., Argane, R., Trauchessec, R., Lecomte, A., & Benzaazoua, M. (2018). Influence of superplasticizers on mechanical properties and workability of cemented paste backfill. *Minerals Engineering*, *116*, 3-14.

Mollah, M. Y. A., Adams, W. J., Schennach, R., & Cocke, D. L. (2000). A review of cement superplasticizer interactions and their models. *Advances in Cement Research*, *12*(4), 153-161.

Mozaffaridana, M. (2011). *Using thermal profiles of cemented paste backfill to predict strength* (Doctoral dissertation).

Orejarena, L., & Fall, M. (2008). Mechanical response of a mine composite material to extreme heat. *Bulletin of Engineering Geology and the Environment*, *67*(3), 387-396.

Ouattara, D., Yahia, A., Mbonimpa, M., & Belem, T. (2017). Effects of superplasticizer on rheological properties of cemented paste backfills. *International Journal of Mineral Processing*, *161*, 28-40.

Ouattara, D., Mbonimpa, M., Yahia, A., & Belem, T. (2018). Assessment of rheological parameters of high density cemented paste backfill mixtures incorporating superplasticizers. *Construction and Building Materials*, *190*, 294-307.

Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003, September). Sulphide reactivity within cemented paste backfill: oxygen consumption test results. In *Proceedings of 56th Canadian geotechnical conference* (pp. 176-183).

Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals engineering*, *19*(5), 407-419.

Pan, H., Yang, Z., & Xu, F. (2016). Study on concrete structure's durability considering the interaction of multi-factors. *Construction and Building Materials*, *118*, 256-261.

Panchal, S., Deb, D., & Sreenivas, T. (2018). Variability in rheology of cemented paste backfill with hydration age, binder and superplasticizer dosages. *Advanced Powder Technology*, *29*(9), 2211-2220.

Pokharel, M., & Fall, M. (2013). Combined influence of sulphate and temperature on the saturated hydraulic conductivity of hardened cemented paste backfill. *Cement and Concrete Composites*, *38*, 21-28.

Prince, W., Edwards-Lajnef, M., & Aïtcin, P. C. (2002). Interaction between ettringite and a polynaphthalene sulfonate superplasticizer in a cementitious paste. *Cement and Concrete Research*, *32*(1), 79-85.

Reid, C., Becaert, V., Aubertin, M., Rosenbaum, R. K., & Deschênes, L. (2009). Life cycle assessment of mine tailings management in Canada. *Journal of Cleaner Production*, *17*(4), 471-479.

Simon, D., Grabinsky, M. W., & Bawden, W. (2011, October). Effect of polycarboxylated acrylic acid polymer-based superplasticizer on cemented paste backfill. In *Proceedings of the Canadian Geotechnical Conference, Toronto, ON, Canada* (pp. 2-6).

Vick, S. G. (1984). A systematic approach to tailings impoundment siting. *Mining Science and Technology*, *1*(4), 285-297.

Wu, D., Fall, M., & Cai, S. J. (2012). Coupled modeling of temperature distribution and evolution in cemented tailings backfill structures that contain mineral admixtures. *Geotechnical and Geological Engineering*, *30*(4), 935-961.

Wu, D., Fall, M., & Cai, S-J, (2014). Numerical modelling of thermally and hydraulically coupled processes in hydrating tailings backfill columns. *International Journal of Mining, Reclamation and Environment 28*(3),173-199.

Wu, A., Wang, Y., Wang, H., Yin, S., & Miao, X. (2015). Coupled effects of cement type and water quality on the properties of cemented paste backfill. *International Journal of Mineral Processing*, *143*, 65-71.

Wu, H. L., Zhang, D., Du, Y. J., & Li, V. C. (2020). Durability of engineered cementitious composite exposed to acid mine drainage. *Cement and Concrete Composites*, *108,* 103550.

Yang, L., Yilmaz, E., Li, J., Liu, H., & Jiang, H. (2018). Effect of superplasticizer type and dosage on fluidity and strength behavior of cemented tailings backfill with different solid contents. *Construction and Building Materials*, *187*, 290-298.

Yin, S., Wu, A., Hu, K., Wang, Y., & Zhang, Y. (2012). The effect of solid components on the rheological and mechanical properties of cemented paste backfill. *Minerals Engineering*, *35*, 61-66.

Zhang, J., Zhang, Q., Sun, Q., Gao, R., Germain, D., & Abro, S. (2015). Surface subsidence control theory and application to backfill coal mining technology. *Environmental Earth Sciences*, *74*(2), 1439-1448.

Chapter 2. Theoretical and Technical Background

2.1. Introduction

This chapter provides a general theoretical and technical background information on the cemented paste backfill (CPB) and the superplasticizers used in its preparation. Section 2.2 introduces the CPB technology, and the different operations involved in its preparation and placement. Various properties of the CPB that are important on its engineering performance are explained in detail under sections 2.3 through 2.5. Finally, section 2.6 provides a review of existing literature on the use of superplasticizers in the preparation of CPB and identifies the research gap being targeted by the current study.

2.2. Cemented paste backfill technology

One of the most important technological innovations in the last three decades, with the aims to increase the productivity of mines, manage tailings cost effectively, contribute to the improvement of safety in mine operations and reduce the environmental footprint of the mining industry is the technology of CPB (Cui and Fall, 2018a,b,c). The technology was introduced in the mining industry in the early 1980s at the Bad Grund mine in Germany and adopted technology in North American mines in the 1990s. In recent years, CPB has become one of the most popular methods for managing milled tailings worldwide (Fall et al., 2015). CPB is a mixture of tailings, water, binder and chemical admixtures when needed. Its components are combined and mixed in a plant usually situated on the mine surface and transported (by gravity and/or pumping) to the underground mine openings (stopes). To carry fresh and hydrating CPB materials during stope filling and thereby prevent CPB from flowing into the mine working areas, retaining wall structures called barricades or bulkheads are built in each of the access ways into the stope prior to filling (Fang and Fall, 2019).

2.2.1 Types of mine backfills

Dry Fills: The dry fills normally consist of smelter slag, underground waste rock, waste rocks from an open pit, gravel, and surface sand. These fills are typically unclassified with the exception to eliminate large boulders. These fills are sent underground normally by dropping a raise into a stope directly from the surface or up to a point where it is pulled to a stope with trucks or LHD (Guyer, 2012). Some of the surface moisture is typically adsorbed by these dry fills. The most suitable sites for dry fills are Avoca or the mechanized fill and cut, or other methods where the requirements for structural backfill are not satisfied (Zhao & Wang, 2017).

Rock Backfill Method is a type of dry fill method. In this method, waste rocks are filled directly on the mining fields at the ground surface after the extraction of economic minerals that result in deeper grounds. This is because the volume and number of voids including goab, goaf, and stopes are increased traditionally (Skrzypkowski, 2018).

Thus, rock backfill can be mentioned as a technology that is involved in transporting backfill forming components like industrial solid waste, soil, gravel, and stone using machinery or gravity equipment or manpower. This technology can be used to fill mined voids present underground and the creation of compressed backfill body (Tailings.info, 2012). The production of backfill material is normally done from waste rocks by mixing, sieving, and crushing by machinery equipment by taking into consideration the distribution of the particle size (Sheshpari, 2015).

One of the most economical backfilling methods is the rock backfill method which is applicable and feasible in some of the cases of underground mining. By this method, the depletion of waste material takes place on the surface which ultimately increases the usable land on the ground (Belem & Benzaazoua, 2004). Thus, environmental pollution is decreased by sending waste rocks to levels at depth which are out of the contact of rain (Hua-zhe, et al., 2011). Also, the stability of the mined area is increased and hence, rock bursts and land subsidence due to changes in the pattern of stress are decreased (Skrzypkowski, 2018).

Hydraulic Backfill Method: This is one of the technologies of refilling in which water is used as the medium of transportation to transfer the hydraulic backfill materials such as crushing sand, mountain sand, river sand, water hydrophilic slag, and waste tailings to fill the voids created underground such as stopes (Cooke, 2001).

In this method, the bulkheads are used to block the mines in which the drainage system is inserted so that water from the backfill comes out of the stope. While there is an increase in the height of hydraulic fill material, there is an accumulation of free water at the top of the backfill top. The solid particles in the hydraulic backfill are classified into: a) Fine particles with diameter less than 75 μm, which together with the conveying water serve as the paste vehicle b) Coarse particles with diameter greater than 75 μm, which are suspended in the vehicle either through turbulence, interparticle contact or the yield stress of the vehicle (Cooke, 2001)..

The fill materials that are used in hydraulic backfill typically have permeability between 10^{-5} to 10^{-6} m/s (Sheshpari, 2015). By the process of gravity, the access water present in the backfill material gets drained (Cooke, 2001). Either non-cemented or cemented backfill can be used in this hydraulic method, but the cheapest method is the non-cemented one when the availability of the waste particles is in a very small size. In designing of barricades and backfill, it is important to apply strict rules so that the properties of backfill material get controlled. Increasingly, hydraulic backfill is being replaced with cemented paste backfill for few reasons. Operationally, large volume of water needs to be pumped out of the hydraulic backfill after the solid particles have settled. Excessive water can cause ponding within stopes, resulting in pipes erosion and barricade failures (Grice, 1998). Also, permeable barricades made of porous concrete bricks are required to allow drainage of excess water (Grice, 1998). Moreover, hydraulic backfill is more or less regarded as a quicksand that is supported by bulkheads. Without proper drainage or dewatering, it has a tendency of undergoing liquefaction, which could pose a huge risk to miners (Stone, 2014).

The grain distribution of hydraulic backfill normally consists of silty sand, and sandy slit. A process known as desliming is used to remove the fractions of clay in which complete material of backfill passes through hydrocyclones by circulation. However, the content of water is reduced by the presence of more solid material in the hydraulic backfill in drained status, but the issue is created when transferred smoothly through pipes (Sheshpari, 2015).

The material used in this method should have a threshold permeability of more than 100mm/h and the backfilled stope's drainage is accelerated when the values are higher. The USA's coal mines in the Wyoming area are an example of this type of backfilling in which voids are created in pillar and bord or pillar and room underground mining methods. In this area, it was applied so that subsidence in coal mines of the United States could be prevented (Sheshpari, 2015).

The outcomes obtained from the Wyoming area's hydraulic backfilling proved that voids that lie below the groundwater table give better results with this method in comparison to dry voids. It has also been found that more backfill material is accepted by mining areas that consist of lower rubblized zones through the conditions of water drainage (Sheshpari, 2015).

Silica-Alumina Based Backfill: (Yao & Sun, 2012) performed research to study novel backfill material based on silica-alumina and composed of fly ash and coal refuse. One of the fastest-growing coal industries in which waste material is produced in a large amount is the coal refuse form (Cui & Wu, 2012). At different temperatures, there are different behaviors of fly ash and coal refuse. With an enhancement in thermal activation temperature varying from 20 to 950 degrees

Centigrade, the coal refuse's pozzolanic and flowability properties are enhanced significantly (Yao & Sun, 2012).

However, fly ash's flowability is decreased at this temperature because of the critical agglomeration conditions on its surface (Yao & Sun, 2012). It has also been proved in research that an optimum ratio obtained at 20 degrees Centigrade with 15% fly ash and 750 degrees Centigrade with 5% coal refuse gives the low bleeding rate, a high compressive strength, and the best flowability in backfill material (Yao & Sun, 2012).

Hardened silica alumina-based backfill structure was analyzed in different places for attributes of toxicity and none of the tested elements was found above the limitations of EPA (Sun & Yao, 2012). It clearly shows that the material used in this backfill method is totally environmentally friendly. The addition of just 1% of the cement to backfill material based on silica and alumina with the rest of the materials just solid waste from industries results in giving the vast potential for savings in the backfill industry's capital expenses (Yao & Sun, 2012).

Cemented Paste Backfill: A non-homogeneous material that is prepared by mixing cement, water, and waste tailings is known as Cemented Paste Backfill (CPB). The proportion of waste to solid is between 70% and 85%, with a hydraulic binder mixed normally between total weight's 3-7% (Sheshpari, 2015).

The preparation of underground backfill materials can be done from various types of binders and aggregates with different methods of placement, transportation, and preparation on the basis of infrastructure, mining method, and fill type. This type of backfill is gaining popularity these days because of its comparatively high rate of delivery, homogenous properties that remain the same as it is placed, and characteristics of tight filling in comparison to other methods of filling (Shahsavari & Grabinsky, 2014).

As mentioned by Yilmaz (2018), understanding the *in-situ* properties of CPB is very important because the development of a well-organized design of mine in terms of security and cost is really essential. In the experiment conducted by Yilmaz (2018), the performance and *in situ* behavior of CPB are analyzed with three different binding agents. It was proved in the results that CPB having slag-based cement presented the highest compressive strength.

As the stope depth increases, the CPB strength also increases mainly because of the enhanced geotechnical properties, such as porosity, degree of saturation, increased retention of specific surface area at the simulated stope's bottom, and decreased water content (Yilmaz, 2018). It has also been proved by geochemical testing that Calcium Ca and Sulphate SO4(-2) enhances as the curing time is increased while it decreases with the increased depth of stope (Yilmaz, 2018).

Cemented backfill is best suited for fill and undercut long hole open stoping, and other methods where the requirement of structural fill is stated. The design criteria of structures of CPB are mainly dependent on durability, environmental performance, barricades stability, and mechanical performance. In CPB, the temperature sources would be friction between transferring pipes, the geographical location where mines are located, gradient temperature of the earth, binder hydration, friction between hosting rock walls and cement paste and cemented paste (Sheshpari, 2015).

In permafrost areas of the earth, a very low temperature is observed during some part of the year which has a huge impact on the temperature of CPB in hydration thermal load, transportation, and surface mixing plants. Seasonal changes result in a change in temperature which considerably influences the temperature of the CPB's water component originating from surface lakes. These changes in temperature of CPB results in significantly affecting the CPB rheological behavior (Sheshpari, 2015).

2.2.2 Design criteria for CPB structures

The mechanical performance, durability, environmental performance, and the stability of the barricades contribute to the design criteria of the CPB (Pokharel and Fall, 2011). The mechanical properties of the CPB ensure that the safety of the mines is secured against buckling or caving in thus avoiding injuries, trapping or the occurrence of death among miners (Pokharel & Fall, 2011). Therefore, the CPB must achieve certain loading requirements which are only made possible during the design process (Fang et al., 2020). The stability of the barricades ensures that the application of fresh and hydrating CPB during the process of filling the stopes does not overflow to the safe working areas of the mines (Pokharel and Fall, 2011).

A mechanical failure of the CPB increases its permeability thus contributing to contamination of the ground water. An increase in applied stress that results from heavy materials placed on top of the mines also leads to the buckling of the CPB which weakens its mechanical stability (Koupouli et al., 2016). The stability of the barricade walls, on the other hand, is dependent on the permeability of the hydrating CPB. On the environmental aspect, the permeability of the CPB is an important factor that ensures that it does not emit harmful materials into the ground water or release toxic chemicals into the mines. Therefore, the permeability of the CPB tends to exert pressure on the durability and performance of the environment around the mines.

The effect of the CPB on the environment is further dependent on the oxidation potential of the tailings (Bull and Fall, 2020a). Tailings that exhibit high potential for oxidation tend to be more harmful to the environment than those with low affinity for oxygen. The reactivity of the tailings is dependent on the ratio of sulfur present and the ability of fluids such as oxygen and water to percolate in the CPB (Klein and Simon, 2006). Water and oxygen tend to heighten the rate of oxidation which can essentially contribute to toxification of the CPB. Moreover, the hydraulic conductivity of the CPB contributes to the deterioration of the environment because it allows groundwater to diffuse through it (Yin et al., 2012). The percolation of water through the CPB potentially leads to the transportation of harmful chemicals that contaminates the ground water.

However, the level of the hydraulic conductivity of the CPB provides essential information such as the availability of cracks or pores in the system (Yin et al., 2012). Cracks and poor pore structures in the CPB indicate that fluids can permeate through it thus hastening oxidation and eventual contamination of the groundwater and the mine. The durability and stability of the CPB tend to be dependent on the curing temperatures and time. The durability and stability aspects of the CPB are measured in terms of its hydraulic conductivity (Roncero et al., 2002).

Research studies on the design criteria of the CPB have indicated that the hydraulic conductivity decreases with the curing period and temperatures. These studies further show that changes in hydraulic conductivity subject to temperatures are more pronounced during the early stages of the curing process (Roncero et al., 2002). Again, it has been observed that the type of the binder used in the formation of CPB affects temperature-related changes of the hydraulic conductivity of the CPB (Roncero et al.2002). In essence, the design criteria of the CPB are informed by its mechanical requirements and environmental performance of the mines as stipulated in policies guiding the operation of mines (Roncero et al., 2002). Furthermore, the time required for the curing of CPB determines the proportion of tailings, binders, and water used in the mixture. The curing temperature also plays a significant role in selecting the design of the CPB (Yin et al., 2012). Areas with cold temperatures have different CPB designs compared to those areas with moderate or high temperatures. However, the design criteria of the CPB revolve around the proportionate mixing of the three components used in its manufacture.

2.2.3 Mix design and preparation

The final tailings obtained from milling are initially thickened to increase solids concentration from 35 wt.% to about 55-60 wt.% (Belem and Benzaazoua, 2008). This is because the tailings are usually in form of a dilute slurry due to the large amount of water added during the milling process. This stage of paste backfill preparation is mostly carried out using a hydro-cyclone to deslime (slimes being the fine particles in the tailings) and dewater the tailings. However, some proportion of fines must be left to improve the paste quality and pump-ability during placement (Jung and Biswas, 2002). For tailings that do not have excess fines, a thickener can directly be used. After thickening, the material is filtered using a disc of vacuum filters generating a moist filter cake that can be transported using belt conveyors (Jung and Biswas, 2002). Flocculants are to facilitate the filtration process. A flow chart of a typical paste backfill plant is presented in Figure 2.1.

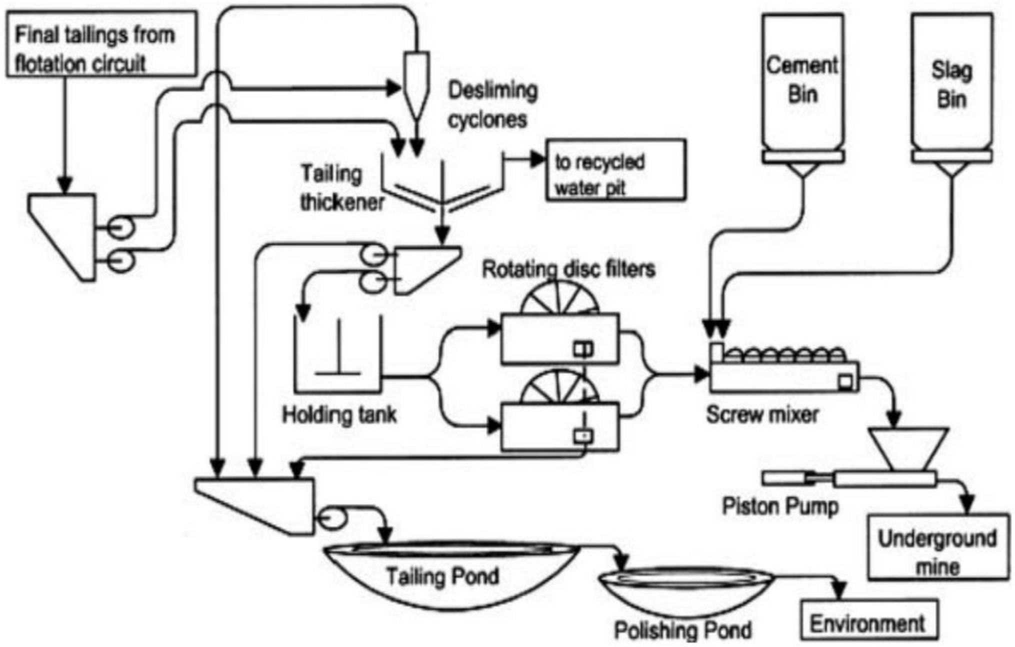


Figure 2.1. Flow chart of a paste backfill plant (Cayotte, 2003)

2.2.4 Cement and hydration process

Portland cement type I (PCI) is the typical binder used in the preparation of CPB. Calcium silicate minerals (i.e., lime, silica, alumina, and iron oxide) are its main raw materials, which undergo pyroprocessing to create a kiln product that becomes a hydraulic cement (Van Oss and Padovani, 2002; Huntzinger and Eatmin, 2009). The major constituents of the kiln product (clinker) that gives the PCI its hydraulic characteristics are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). Although there are other compounds in the final cement product, the silicates and aluminates are largely responsible for the hydration reaction of the PCI (Bergold et al., 2017). Hydration occurs when these compounds come in contact with water, generating new products that are responsible for the setting and hardening of the mixture. Cement hydration is a continuous irreversible process that can continue for a very long time as long as there are unhydrated cement and water available.

2.2.5 Transportation of CPB

Figure 2.2 below shows the CBP transportation system with the influence of thermal factors and their transfer to underground voids. In every single underground mine, the transportation system of backfill is different as far as different temperatures are concerned (Wu & Fall, 2013). Fresh CPB is typically transported from the mixing plant on the ground surface into the voids either by gravity and/or under pressure through a pipe system (Roshani and Fall, 2020).

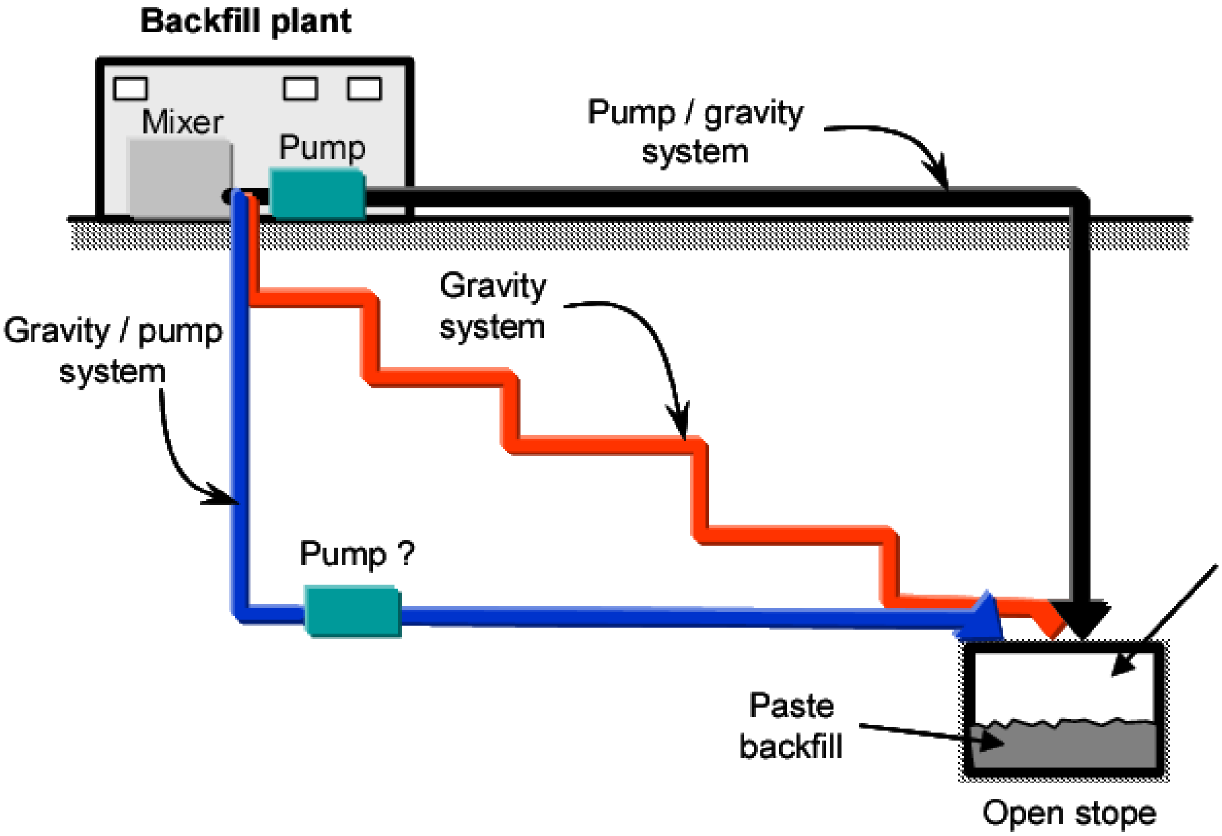


Figure 2.2. Transportation system of CBP to underground voids (Belem and Benzaazoua, 2004)

2.3. Admixtures used in CPB

Chemical admixtures are added to cementitious materials such as concrete and paste backfill to change one or more of its essential properties. Commonly, the admixture can improve the quality of the material, its setting time, workability (rheology) or change its setting time. Some of the basic admixtures use in recent days are summarized below.

2.3.1. Accelerators

These admixtures are added to concrete for the purpose of increasing the rate of cement hydration thereby shortening the setting time. This in turn results in an increase in early strength gain that may be required in certain circumstances. The chemical composition of accelerating admixtures includes inorganic compounds such as carbonates and fluosilicates as well as organic compounds such as triethanolamine (Bhatty, 1991).

2.3.2 Plasticizers (low range water-reducing agents)

Coded as type A in ASTM 494, water reducing admixtures are used to modify the property of cementitious material by lowering the water to cement ratio requirement (Mbugua et al., 2016). Their use is derived by the need to maintain workability while at same time not jeopardizing its essential properties especially mechanical strength. Plasticizers have the capability of reducing the water content 5 to 12% (ASTM, 2017).

2.3.3 Superplasticizers (high range water-reducing admixtures)

Admixtures that are capable of reducing the water content in the cementitious material by 12% or higher are classified as superplasticizers (ASTM, 2017). The time during which a cementitious material retains its fluidity (flow time) depends on the dosage of the superplasticizer. Figure 2.3 show the variation of the flow time with the dosages of a superplasticizer used. Commonly used superplasticizers are classified into four main groups, namely sulphated naphthalene formaldehyde, sulphated melamine formaldehyde, vinyl copolymers, and polycarboxylic ethers.

2.3.3.1 Sulphated naphthalene formaldehyde

Also called polynaphthalene sulphonates (PNS), these superplasticizers were first introduced as concrete admixtures in the late 1960s (Gelardi et al., 2016). They are produced through sulphonation of naphthalene with sulphuric acid, resulting in a molecular structure shown in Figure 2.4. They have a varying molecular weight based on their condensation number (n), which varies bwteen 1000 to 2000 (Edmeades and Hwelett, 1998). Studies have shown that PNSs have an advantage of not altering the stability of pore network in an air-entrained concrete with freeze-thaw resistance, making them widely used in North America (Nkinamubanzi et al., 2016).

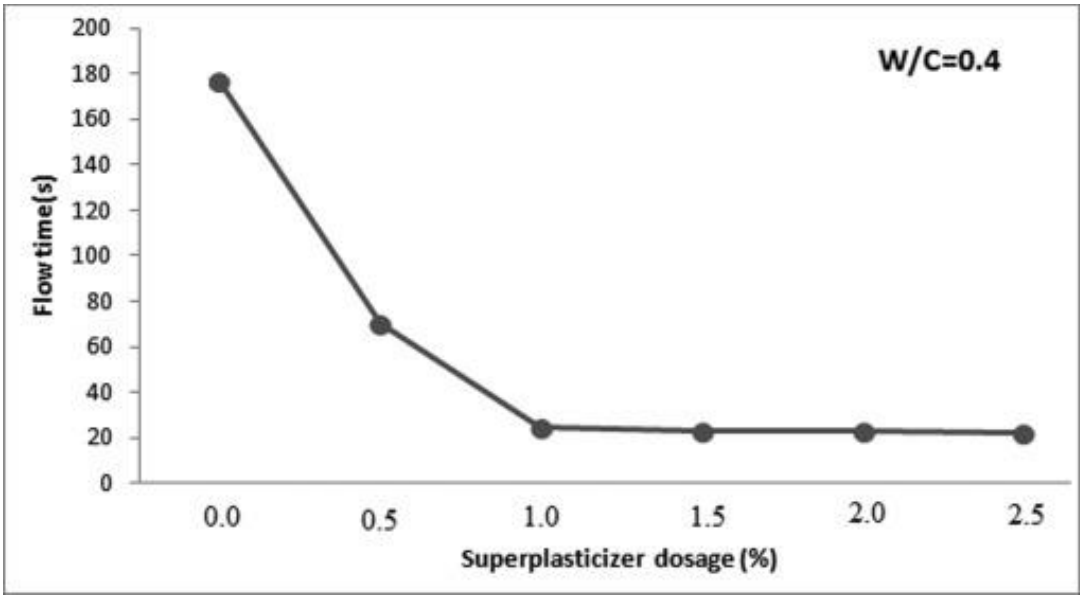


Figure 2.3 Variation of the flow time for various superplasticizer dosages (Benaicha, 2015)

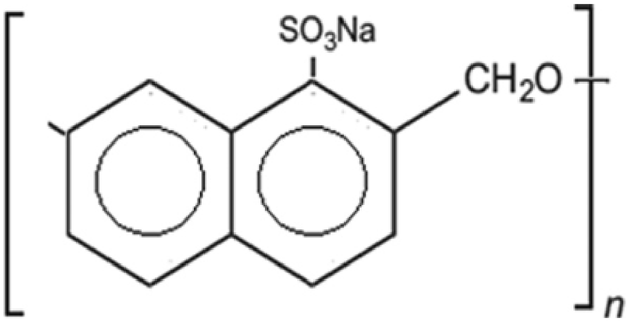


Figure 2.4. Structural formula of sulphonated naphthalene formaldehyde (Aicha, 2020)

2.3.3.2 Sulphated melamine formaldehyde

Also known as polymelamine sulphonates (PMS), these superplasticizers were developed in Germany and commercialized in 1964 (Edmeades and Hwelett, 1998). They are made up of synthetic polymers that have a structural formula with a repeating sulphonate group as shown in Figure 2.5. Synthesis of PMS involve the conversion melamine to trimethyl, which is then treated with formaldehyde (Aicha, 2020). Their condensation number varies between 12,000 to 15,000, which determines their molecular weight (Darweesh, 2016).

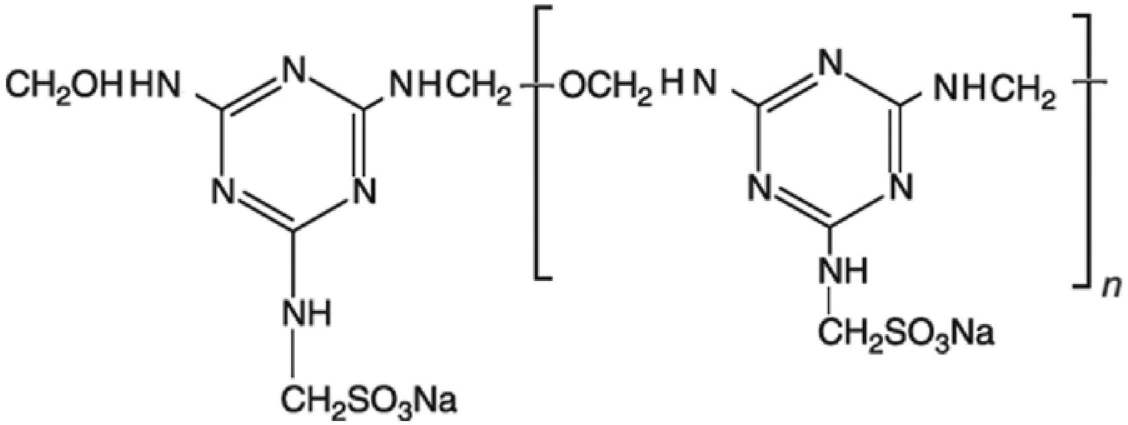


Figure 2.5. Structural formula of sulphonated melamine formaldehyde (Aicha, 2020)

2.3.3.3 Vinyl copolymers

These types of superplasticizers are produced from the radical copolymerization of various monomers, namely polyethylene glycol acrylate, polyethylene glycol biester of maleic acid and citric acid, acrylic acid, sodium allylsulphonate, and methyl acrylate (Lu et al., 2010). The general structure of the vinyl copolymer superplasticizer is shown in Figure 2.6. The advent of these polymer-based superplasticizers paved way to the revolutionary high-range water reducers with long side chains (AIcha, 2020).

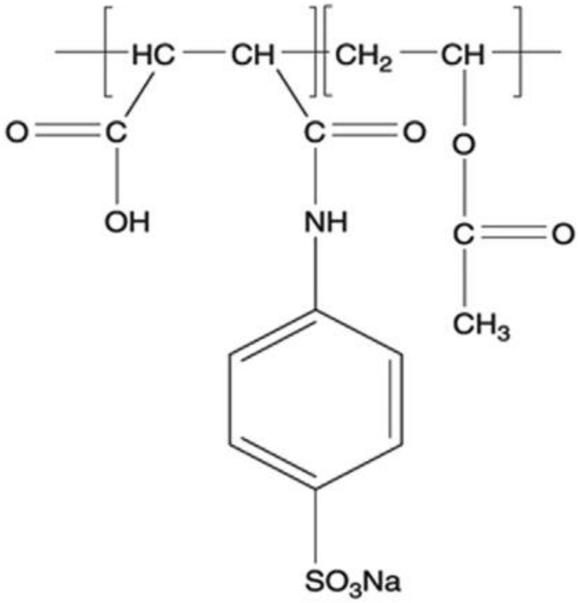


Figure 2.6. Structural formula of vinyl copolymer superplasticizer (Aicha, 2020)

2.3.3.4 Polycarboxilic ethers

Introduced in the 1980s, these superplasticizers fall under the most recent generation of polymer-based water reducers with a comb-like structure (Stengel and Schießl, 2014). Their general molecular formula is shown in Figure 2.7. They contain polymer groups with polyoxyalkylene (e.g. polyethylene), carboxylic acid, and carboxylic acid anhydride monmers (e.g. methacrylic acid) (Stengel and Schießl, 2014). They are produced either through esterification, which yields random copolymer chains, or by aqueous free copolymerization, which yields gradient polymers with higher side-chain density (Aicha, 2020). Their advantage over other types of superplasticizers includes flexible molecular structure, low dosage requirement, high water-reducing capability and environmental friendliness (Zhang et al., 2021).

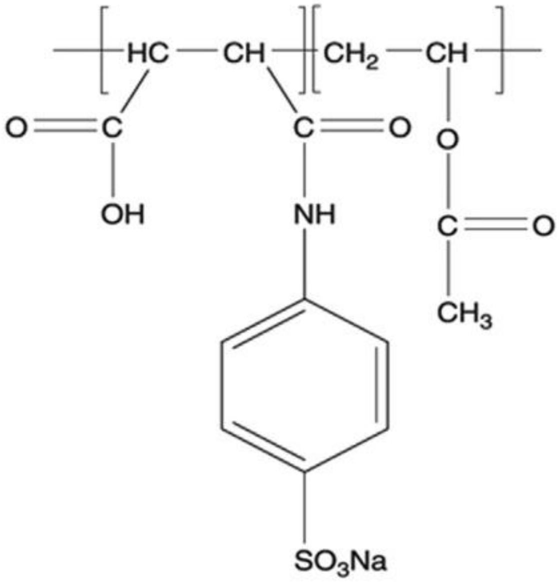
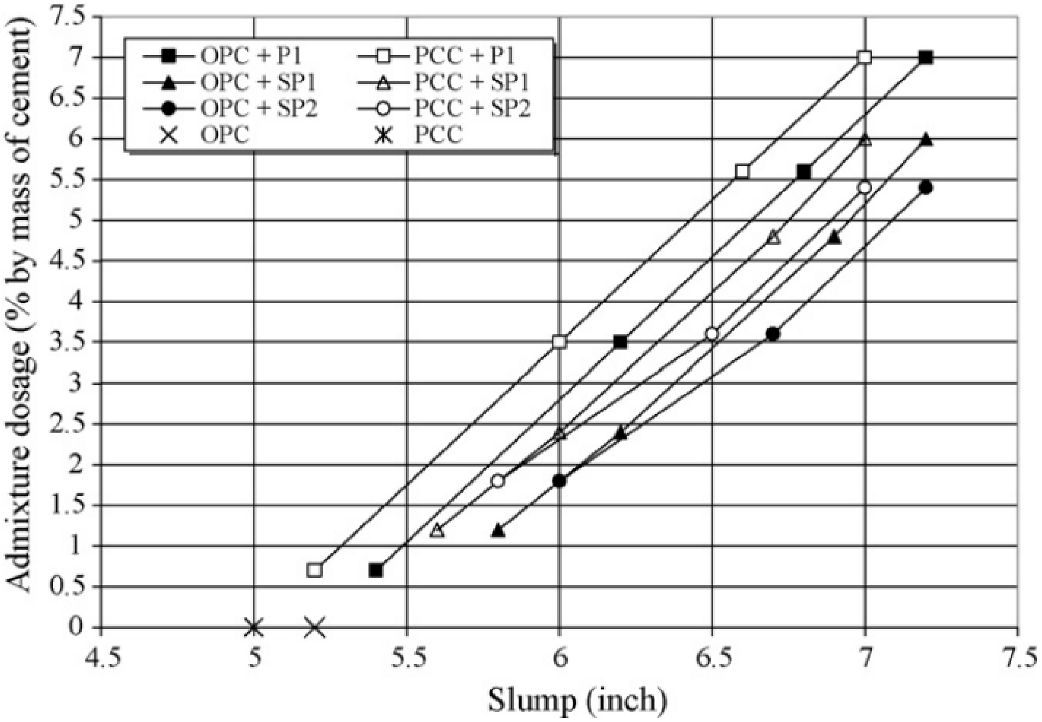


Figure 2.7. Structural formula of polycarboxilic ether (Aicha, 2020)

2.3.4. Effects of admixtures on the properties of CPB

The use of plasticizers and superplasticizers or simply water-reducing admixtures tends to elevate the strength of concretes without the addition of the binders (Agulló et al., 1999). Some of the widely used water-reducing admixtures include naphthalene, sulfonate, lignosulphonate, and polycarboxylates. These admixtures essentially reduce the water content in concretes by a significant percentage. Furthermore, the admixtures contribute to the improvement of the uniaxial compressive strength of the CPB (Cyr et al., 2000). However, the effect of the plasticizers on the strength of the backfills is dependent on the proportion of the binder in the CPB. The use of the water –reducing admixtures assists in the alleviation of a possible reduction in the strength of the CPB (Cyr et al., 2000). The higher water-cement ratio is required to move the cement paste from the manufacturing plant to the tunnels of the underground mines.

The use of water-reducing admixtures thus elevates the removal of water from the paste thus improving the strength and the stability of the CPB (Ercikdi et al., 2010). A high water-cement ratio for tailings with high contents of sulfide tends to weaken both the short and the long-term mechanical characteristics of the CPB. Research studies on the effect of plasticizers on the mechanical properties of the CPB indicate that the use of water-reducing admixtures effectively improves the strength and the consistency of the CPB (Ercikdi et al., 2010). However, as indicated before, the effectiveness of water-reducing admixtures is dependent on the type of the binder and the admixture employed. A study done by Ercikdi et al. (2010) showed that the use of water-reducing admixtures alleviates the challenges faced with the higher water-cement ratio in sulphide-based tailings (Ercikdi et al., 2010). Figures 2.8 and 2.9 show the influence of the water reducing admixtures on the rheology and strength of CPB obtained by the authors. Khan, Nuruddin, Ayub, and Shafiq (2014) postulated that admixtures improve the mechanical and rheological characteristics of cement paste due to their inherent characteristics (Khan et al., 2014). The writers assert that admixtures essentially tend to improve the hardening properties of concretes. The researcher specifically enumerates the benefits of mineral admixtures where they observe that they influence the rheological properties of cement pastes. They further observe that the influence of the mineral admixtures on the rheological properties of fresh concrete at the time of preparing and hardening of the concrete happens in some ways (Khan et al., 2014).



Note: P1 is a water reducer made of lignin, SP2 made of poly naphthalene sulfonate condensate, and SP2 made of polycarboxylate condensate)

Figure 2.8. Influence of water reducing admixtures on the rheology of CPB samples (Ercikdi et al., 2010)

According to the researchers, mineral admixtures affect the water demands, setting time, the heat of hydration, reactivity, and bleeding of the concrete. In their view, the influence of mineral admixtures on the rheological properties of the cement pastes contributes to the mechanical properties and durability of the concrete (Khan et al., 2014). The use of natural pozzolans as admixtures is further emphasized by several researchers such as Ercikdi et al. (2010) in their journal article “Effect of Natural Pozzolans as Mineral Admixture on the Performance of Cemented-Paste Backfill of Sulphide-Rich Tailings.” These researchers argue that pozzolans constitute of inherent natural characteristics that influence both the rheological and mechanical properties of concrete. The pozzolans tend to have a higher content of silica which is the main component that elevates the uniaxial and rheological properties of concrete (Ercikdi et al., 2010).

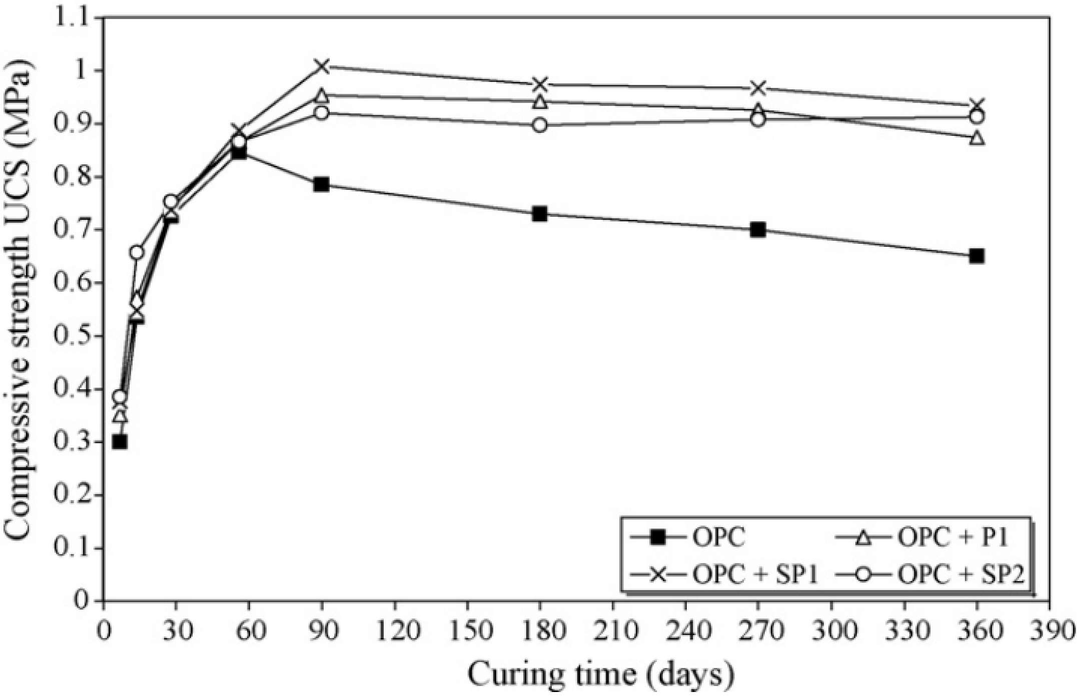


Figure 2.9. Influence of water reducing admixtures on the mechanical strength of CPB samples (Ercikdi et al., 2010)

However, the researchers add that the effectiveness of pozzolans is dependent on the level of their pozzolanic characteristics (Ercikdi et al., 2010). In other words, the higher the content of silica in a pozzolan, the higher the efficacy of its influence on both the mechanical and rheological properties of the concrete. Külekç et al., (2016) argue that waste bricks that are rich in silica and alumina can be used effectively as admixtures. The researchers postulate that waste bricks are made of clay which tends to be highly reactive when burnt at high temperatures. Furthermore, the clay products improve the pore size distribution and the overall porosity of CPB due to the ability of the clay to ground to fine particles when burnt at high temperatures. Improved porosity leads to a reduction of permeability of the CPB. Therefore, the use of the waste bricks significantly improves the compressive strength of CPB while at the same time resisting the oxidation of the sulfides present in tailings (Külekçi, et al., 2016).

The characteristics exhibited by the waste bricks in the improvement of the mechanical properties of CPB are credited to the pozzolanic reaction that occurs due to the presence of silica and alumina (Külekçi et al., 2016). The use of admixtures further affects thermal properties of the CPB. Celestine and Fall (2009) argue that different admixtures inject different thermal characteristics into the CPB. The use of admixtures with higher properties of thermal conductivity tends to improve the overall thermal conductivity of the CPB. On the other hand, the use of admixtures with low qualities of thermal conductivity tends to reduce the thermal properties of the CPB (Célestin and Fall, 2009).

2.4 Rheological properties of CPB

2.4.1 Definition of yield stress and viscosity

Viscous fluids such as CPB and mortar can only deform indefinitely if subjected to an amount of stress above a certain critical value. Below that stress, the materials deform finitely or elastically in a similar way like solids (Coussot, 2014). Yield stress of a paste is, therefore, defined as the stress that must be applied before it begins to flow (Larson, 1999). Fluids that exhibit yield stress are structurally made up of different dispersed components that continuously interact with one another (Larsson and Duffy, 2013). According to De Kee (2021), the behaviour of these type of fluid cannot be represented by a straight line on a shear stress versus shear rate plot.

Viscosity is a measure of the fluid’s resistance to flow. More specifically, viscosity refers to the resistance of a fluid towards being deformed when subjected to a shearing force (Wong, 2013). The apparent viscosity of fluids is typically given as the applied shear stress divided by the shearing rate with a unit of Pascal-second (Pa.S). For non-Newtonian fluids, the apparent viscosity is not constant, so the viscosity is specified for a given shear rate (Partal and Franco, 2010).

2.4.2 Yield stress of CPB

Yield stress is the commonly used parameter to evaluate the flowability and transportability of fresh CPB. It is used to determine how much pressure is required to effectively pump the CPB from the mixing plant into the underground mine stopes. Haiqiang et al. (2016) probed the effects of time and above zero temperatures on the yield stress of CPB. Their investigation revealed that CBP samples at room temperature had higher yield stress values than the ones in sub-zero temperatures. In addition, they have found that the yield stress values depend on the mixed components of CPB. Particle size distribution (PSD), the density of the particle, and concentration of slurry also contribute to the yield stress of CPB according to Cheng et al. (2020). The paste stability coefficient (PSC) was found to unify the rheological model, which is applicable to various materials used in mines. The study of Cheng et. al. (2020) regarding CPB technology revealed that increased time decreases the plastic viscosity while simultaneously decreasing the yield stress of CPB at an exponential negative rate.

In another study, the tailings' geotechnical characterization includes specific gravity, plastic limit, liquid limit, and grain size distribution. On the one hand, the rheological properties of the CPB include slump, yield stress, saturated density, and solid content. It has been found that the increased solid content influences the yield stress and the saturated density; however, the slump is decreased (Niroshan et al., 2018). Jiang and Fall (2017) stress that salinity also influences the yield stress of CPB in a sub-zero environment. Results showed that increased salinity also increases the flowability of the yield stress of CPB. Ouattara et al. (2017) argued that the fluidity of CPB may be aided by an increased superplasticizer, especially in temperatures of elevated mining environments. According to Kou et. al. (2020), alkali-activated slag significantly affects the yield stress and rheological properties of CPB. CPB mixtures have been examined using the

Bingham model and the researchers found that the alkali-activated slag (AAS) causes increased rheological behavior. Moreover, AAS is shown to be very sensitive to curing temperatures. Future studies are recommended by the authors to extend the research on CPB and the use of AAS for the improvement of mining processes.

With respect to the rheology of CPB, Xiaoping et al. (2019) highlighted that sulfate can cause significant changes irrespective of the curing time. Hence, sulfate can influence the yield stress regardless of time, which most authors argue is a vital influence. The more sulfate is introduced in CPB, the more the viscosity of CPB increases. More so, the yield stress decreases as the sulfate content increases. When CPB is transported to the pipelines, sulfate is an important optimization component. Qi et al. (2018) agree that mixed properties influence the yield stress of CPB. Aside from mixtures, mechanical properties are also vital. The researchers emphasized the importance of machine learning (ML) and genetic algorithms (GA) to determine CPB yield stress.

2.4.3 Viscosity

Different factors can affect the viscosity of CPB, which is also an important parameter for assessing flowability. Deng et al. (2018) studied the role of CPB of particle size on the rheological properties of CPB. The larger the size of the particles, the higher the viscosity of CPB. The authors shared the importance of understanding the influence of size in mining processes citing that packing density is essential for efficient transport of the mining materials. Cao et al. (2018) also focus on the distribution of materials and the importance of evaluating the particle size before transport. These two studies agree that the viscosity of CPB depends on particle size and packing density. In addition, the slurry of cemented tailings backfill, along with the cement-to-tailings ratio (c/t), and solid content (SD) also need to be examined to get the viscosity of the materials used as this will ensure cost-efficiency of operations.

Yan et. al. (2019) argue that a mixed hydroponic agent will be essential in the construction process along with ensuring the dewatering efficiency. This comes along with the viscosity of the CFB slurry. The researchers recommend that water-based agents are easy to combine and very effective. This study is intended to improve the dewatering process as well as CPB gelation efficiency. Future studies are recommended to ensure that the efficiency of dewatering and gelation will be maintained or improved. Tkach et al. (2015) support the importance of hydroponic agents or specifically water-repellent concrete in improving construction processes. Determining the plastic viscosity is vital for the evaluation of CPB so that the "geotechnical stability of underground mine" will be improved. Panchal et al. (2018) explain the importance of hydration age, SP dosages, and binder on the whole process as well as the Fluidity Index in order to reduce negative rheological properties. Another study by Wu and Cai (2015) supplements the importance of hydraulic behavior through cement hydration. The authors also note the role of temperature in successfully applying these processes in the cemented tailings backfill.

According to Xue et al. (2020), viscosity is affected if the temperature is at 20 to 60 °C. The higher the temperature, the lower the viscosity. And the lower the viscosity, the lower the level of yield stress as well, which affects the CPB. The authors, like most of the authors in this review, believe that temperature is a significant factor that affects viscosity. Wang et al., (2019) believe that the use of focused beam reflectance measurement (FBRM) as a tool for measuring the rheological properties, namely viscosity, thixotropy, and yield stress is deemed accurate. More importantly, rheological behavior changes will be monitored and evaluated more efficiently using the tool. For long-distance pipeline transportation, the accuracy of the evaluation of rheological behavior is extremely important to save costs and ensure safety (Wu et al. 2018). According to Qian et. al. (2018), the use of polycarboxylate ether superplasticizer (PCE) is recommended to ensure critical micelle concentration (CMC). CMC is highly suggested by the researchers to increase viscosity and improve other rheological properties necessary to ensure the efficiency of construction and mining processes.

2.5 Mechanical properties of CPB

Mechanical properties, such as compressive and shear strength, are vital towards proper design of stable and safe backfill structures. Similar to other cementitious materials, CPB is prepared in a paste form and then transported and placed into the underground stopes. It then begins to harden gradually owing to the reduction of pore water and the hydration of the incorporated binder (Newman and Choo, 2003; Benzaazoua et al., 2004). Through that, the backfill structure gains appreciable strength that allows it to stabilise the surrounding rock mass provides ground support for the mining operations to continue (Shahsavari and Grabinsky, 2016; Ahmed and Moghaddam, 2017). A ground failure due to improper backfilling process or weak structure can lead to unnecessary delay and may oftentimes put miners at risks of injuries or loss of lives (Bloss, 2014; Zhao et al., 2020). Therefore, it is pertinent to design CPB structures with adequate mechanical strength properties that ensure short- and long-term stability. Three typical mechanical properties considered in the CPB design, namely stress-strain behaviour, unconfined compressive strength, and shear strength are discussed in this section.

2.5.1 Stress-strain behaviour

The response of CPB structure under load is known to be governed, to a considerable extent, by the stress-strain relationship similar to other construction materials (Ting et al., 2020). It is critical to understand the stress-strain behavior in the compression because the CPB structures are mainly subjected to compression during service. The precise form of the stress–strain relationship is largely dependent on the constituents of the CPB material and some external factors in the confinement (Ghirian and Fall, 2014; Doherty et al., 2015). In fact, different stress-strain behaviours exist between confined and unconfined CPB structures (Jafari et al., 2020).

The typical stress-strain behaviour of CPB under axial compression with different deformation stages is shown in Figure 2.10 (Wu et al., 2019). The first segment (o-a) represents the deformation of the CPB due to pore compaction and it is concave in shape. It is followed by an approximately linear segment (a-b) in which the specimen undergoes an elastic deformation. The next stage (b-c) just before the peak is the localized deformation with a convex stress-strain curve. It is where the material undergoes yielding, separating the elastic deformation from the failure or plastic deformation (Want et al., 2021). After that, the CPB undergoes a stress softening during which the main load framework is destroyed (segment c-d). Finally, the specimen undergoes what is known as residual strength deformation (d-e) in which only small axial load is supported by the few unbroken bonded elements. Nevertheless, the actual nature of the deformation curve for any CPB specimen and how long each stage elapses during the compressive loading depends on several factors, among which are: curing age, type and content of the cementing material, size and gradation of the tailings, drainage, and curing stress (Belem et al., 2000; Ghirian and Fall, 2016; Qiu et al., 2017).

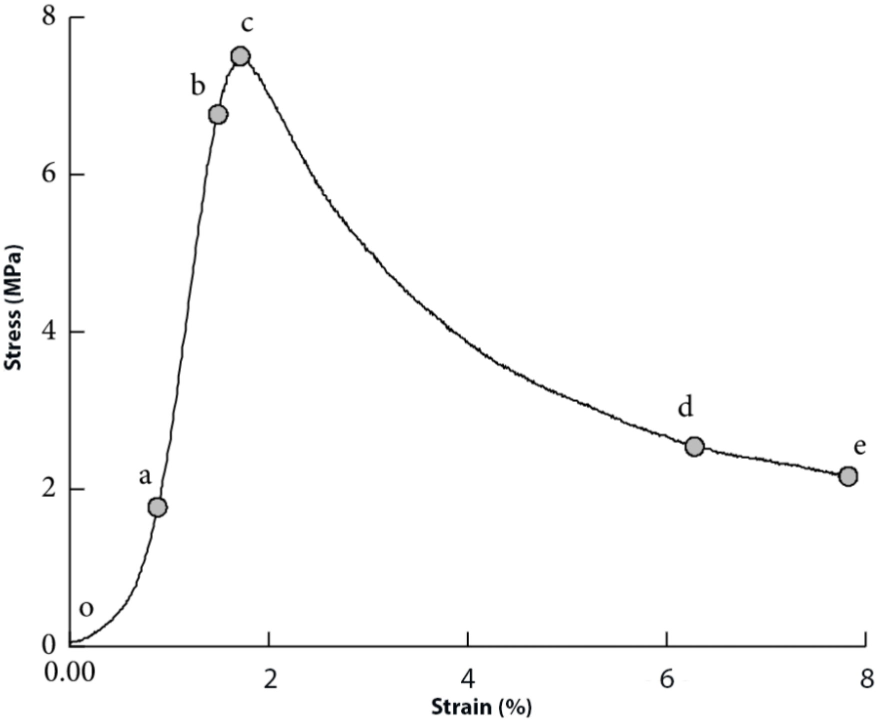


Figure 2.10. A typical stress-strain curve of CPB specimen under axial compression (Wu et al., 2019)

Based on experimental study by Wang et al. (2021), the deformation of CPB at early age is usually gradual with a continuous yield failure being dominant. This can be observed on the 5 days and 7 days stress-strain curves in Figure 2.11 with no sudden post-peak fall. However, the CPB deformation curves for samples cured for 7, 14, and 21 days exhibit a short yield period before the post-peak fall. Beyond 21 days, the CPB specimens show a prominent peak or ultimate failure points that occur right after the elastic deformation. It follows that for the CPB cured at age below 7 days, the deformation behaviour is mainly plastic with elongated yield om the stress-strain curve.

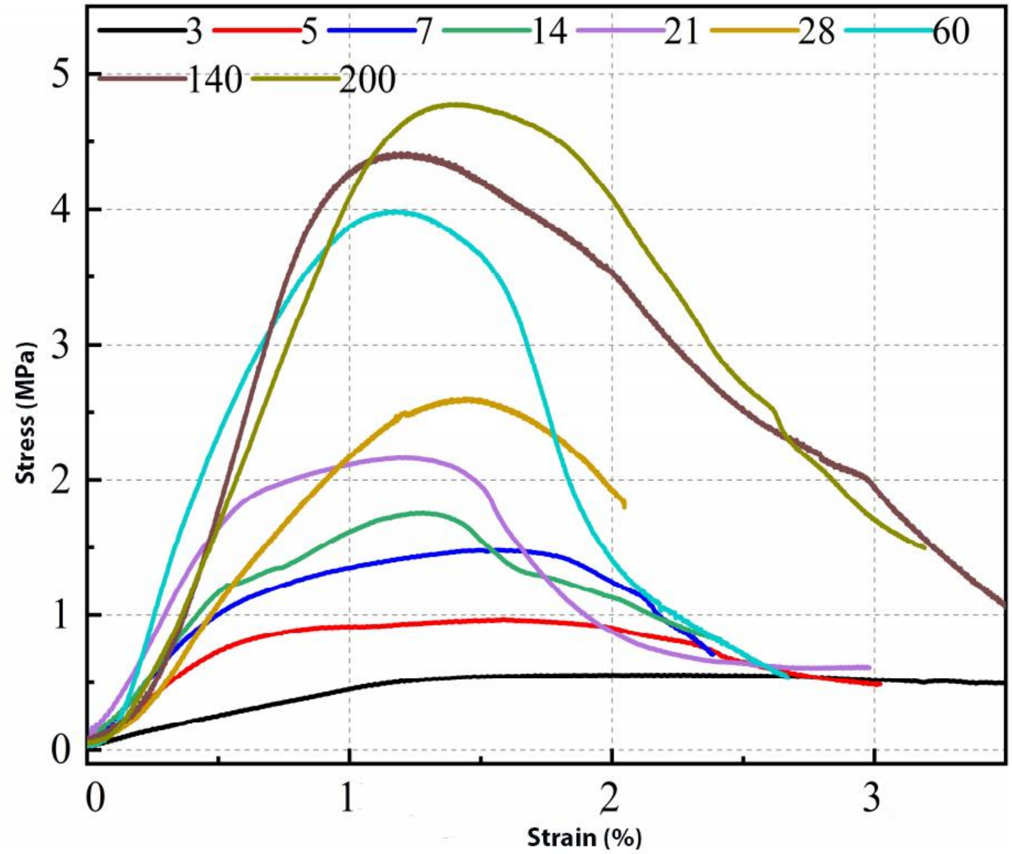


Figure 2.11. Stress-strain curves of CPB at different curing ages from compression test (Wang et al., 2021)

2.5.2 Unconfined compressive strength

The type of binder material used in the manufacture of CPB further determines its mechanical properties. The uniaxial compressive strength of the CPB backfills is also significantly influenced by the percentage of artificial or natural porous materials used to produce the CPB (Fall et al., 2008). In essence, an increase in porosity tends to decrease the uniaxial compressive strength of the backfill materials. The porosity of the CPB can be decreased by using fine or relatively fine materials as the tailings. Jian-et al. (2016) show that the curing age, cement-sand ratio, and the solid phase mass fraction have an impact on the uniaxial compressive strength of the CPB (Fu et al., 2016). However, the three researchers postulate that the three factors influence the strength of the CPB differently. Fu, song, and Tan observed that the uniaxial compressive strength of the CPB increases exponentially when the solid phase mass fraction increases (Fu et al., 2016). However, the observation mentioned above is only possible when both the curing age and the cement sand ratios are constant. Their research on factors that influences the strength of the CPB backfills further indicated that the uniaxial compressive strength increases exponentially with an increase in the curing age when all the necessary conditions are maintained (Fu et al., 2016).

2.5.3 Shear strength characteristics

The shear response of CPB is an important parameter for the design of a mechanically stable backfill structure. As a solid material, the shear strength parameters of CPB are generally expressed in terms of cohesion and internal friction angle (Komurlu et al., 2017; Lingga and Apel, 2018; Xiu et al., 2021). Several factors affect the shear strength characteristics of CPB, such as self-weight, temperature, or sulfate ions. Laboratory experiments and numerical modeling have been used to study the shear characteristics of CPB under different conditions (Rankine and Sivakugan, 2007; Wang et al., 2019; Zhang et al., 2022).

Kormurlu et al. (2017) studied the effects of binder content and curing time on the cohesion and internal friction angle of CPB mass. The shear parameters were measured experimentally using a conventional direct shear box equipment. They observed that the cohesion of the CPB generally increases with an increase of the curing time while the internal friction angle decreases with time. It was also observed that the internal friction angle is the major determinant of the CPB strength in the early age, during which the cohesion between the solid particles is very low. As the CPB ages, cement hydration significantly improves the cohesion. For CPB containing sulphide-bearing tailings, it was observed that the shear strength continues to increase until sulphate attack kicks in. In another study, De Araujo et al. (2017) investigated the effects of high confining pressure on the shear characteristics of CPB. They used self-weight consolidation and rotating wheel methods to simulate zero gravity while exerting high pressure on the CPB structure. The findings show that the strength achieved at high binder content increased up to 400% under the confining pressure.

2.6 Environmental performance of CPB

2.6.1 Acid mine drainage

Exposed suphide-bearing materials such as tailings or waste rocks can interact with the atmosphere to produce toxic compounds in the form of sulphuric acid, dissolved iron, or ferric hydroxides. This process, which may be accelerated by acidophilic iron-oxidizing bacteria is known as acid mine drainage (AMD) (Latan, 2021). According to Park et al. (2019), acid mine drainage (AMD) is one of the most serious environmental threats associated with minerals extraction. Some existing remediation strategies are biological mediation, ion exchange, absorption, neutralization, electrochemical approach, and membrane technology. Naidu et al. (2019) argue that such strategies are unsustainable and require the use of numerous chemical compounds to perform. Reuse of water and recovery of resources may offset the costs of AMD treatments. The researchers found that utilizing membranes can be a breakthrough treatment strategy for AMD treatment. Yet, the process can be costly. Skousen et al. (2018) suggest that mine planners should be able to accurately predict the potential of AMD before it can cause health and environmental disturbance and ensure ethical mining operations at all costs. The authors believe that the focus should be on prevention rather than the treatment strategies if the stakeholders aim for sustainability (Rezaie and Anderson, 2020).

Rezaie and Anderson (2020) agree that sustainable solutions must be in place to minimize the environmental hazards of AMD. The authors assert the importance of lawmakers and the government in regulating AMDs and providing stricter sanctions for violators. Kefeni et al. (2017)

believe that rather than treatment, prevention strategies should be at the forefront. It is true that AMD has huge economic benefits as it can extract sulphuric acid, sulphur, ferrite, ferric hydroxide, and some earth metals necessary for industrial processes but if the environment is harmed, the future is bleak not just for the environment and public health but also the mining industry.

According to research done by Rambabu, Banat, and Pham et. al. (2020), active and passive biological treatment methods need to be re-examined for efficacy as they have found some gaps in bioremediation. Bioreactors may offer faster treatment, but the financial costs are high. Moreover, the treatment process may prove to be unsustainable which can harm the economic status of mining industries in the future. Tomiyama et al. (2019) suggest the use of a combination of geochemical, hydrological, isotopic, and geological techniques to elucidate AMD. Xu et al. (2020) agree that a combination of techniques may prove to be cost-effective. In a highly contaminated area, the team discovered that increasing drainage, preventing dissolved oxygen and sulphur from mixing, and using isotopic fractionation can help treat AMD.

Dutta et al. (2020) argue that cytotoxicity needs to be performed by mining planners often to understand the extent of damage or pollution caused by AMD. More so, nano-limestone has been found to be an effective AMD management. Open-cast mining must be regulated and re-evaluated properly by the government as it is extremely harmful to the environment. It can produce AMD in large amounts caused by pyrite and sulphur oxidation. Igarashi, Herrera, and Uchiyama (2020), on the other hand, suggest a ferrite-formation process that involves as little as two steps which is a neutralization technique to help minimize pollution caused by AMD. The steps involved are copper, arsenic, and zinc removal and ferritization with coexisting ions. The authors strongly believe that such a method is sustainable and environmentally beneficial.

2.6.2 Reactivity of CPB

Chemical reactivity is key to the environmental performance of CPB as it controls the type and concentration of toxic substances generated. Generally, the major sources of chemical reaction in CPB are the sulphidic tailings, which are the predominant waste generated from the mining of many minerals (Lottermoser, 2010; Lindsay et al., 2015). Under atmospheric conditions, the sulphide compounds in the tailings or CPB (commonly pyrite and pyrrhotite) undergo an oxidation reaction to form AMD, emitting toxic elements into the environment (Ouellet et al., 2006; Hamberg, 2015). Upon exposure to the atmosphere through mining, they react with water and oxygen to produce sulfuric acid in the presence of acidophilic microorganisms (Jacobs & Testa, 2014). Jennings et al. (2008) outlined the step-by-step chemical reactions during pyrite (FeS_2 – one of the most commonly occurring sulphide mineral) oxidation process as shown below.

$$2\mathrm{FeS}_{2(\mathrm{s})} + 7\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{Fe}^{2+} + 4S\mathrm{O}^{2-}_{4(\mathrm{aq})} + 4\mathrm{H}^{+}_{(\mathrm{aq})} \qquad equation\ 2.1$$

$$4\mathrm{Fe}^{2+}_{(\mathrm{aq})} + \mathrm{O}_2 + 4\mathrm{H}^{+}_{(\mathrm{aq})} \rightarrow 4\mathrm{Fe}^{3+}_{(\mathrm{aq})} + 2\mathrm{H}_2\mathrm{O} \qquad equation\ 2.2$$

$$2Fe^{3+} + 6\mathrm{H}_2\mathrm{O} \rightleftharpoons 2\mathrm{Fe(OH)}_{3(\mathrm{s})} + 6\mathrm{H}^{+}_{(\mathrm{aq})} \qquad equation\ 3$$

$$14Fe^{3+} + \mathrm{FeS}_{2(\mathrm{s})} + 8\mathrm{H}_2\mathrm{O} \rightarrow 15\mathrm{Fe}^{2+}_{(\mathrm{aq})} + 2\mathrm{SO}_4^{2-} + 16\mathrm{H}^{+}_{(\mathrm{aq})} \qquad equation\ 2.4$$

The kinetics of each of the stage of the reaction usually vary based on the prevailing conditions in the tailings. For example, factors such as degree of saturation, type of sulphide mineral, minerology of the tailings, temperature, pH of the pore water, and oxygen concentration can significantly affect the rate of each of the reactions (Sasaki et al., 1995; Blowes et al., 2003; Druschel et al., 2004).

2.6.3 Leachability of CPB

Leachability refers to the process through which toxic minerals present in CPB are dissolved into percolating water thus transporting them to the reservoirs of the ground water leading to contamination (Deschamps et al., 2008). The leachability of the cemented tailings is dependent on the hydraulic conductivity of the CPB. The rate of hydraulic conductivity of the CPB, on the other hand, is dependent on some other factors. These factors range from the porosity to mechanical failures of the CPB. The use of granular materials or tailings increases the porosity of the backfills and thus elevates its permeability (Deschamps et al., 2008). Furthermore, the proportion of the binding substance in the CPB contributes significantly to its overall porosity. In essence, high porosity in CPB can be attributed to the use of granular materials and a limited proportion of the binder. On the other hand, employment use of fine materials and higher proportions of the binder material in the CPB results to reduced porosity which leads to decreased permeability (Ichrak et al., 2016). Again, cracks emanating from the mechanical failures of the CPB leads lead to increased permeability. In essence, increased permeability or hydraulic conductivity of the CPB increases the rate of percolation of water which dissolves the minerals that contaminate the underground water (Ichrak, et al., 2016).

The leaching of the minerals into the underground water does not necessarily have to be done through the percolation of liquid or water into the CPB. It must be understood that most of the minerals found in the tailings and those that are added to the CPB as admixtures can easily dissolve in water (Ichrak et al., 2016). Therefore, water flowing on the surface of the dry CPB tends to weather the concrete material through dissolution or chemical reactions. The presence of acidic materials and relatively high temperatures hastens the chemical weathering of the CPB thus contributing to the contamination of the mining environment (MEND, 2006). Furthermore, the presence of necessary conditions in underground mines might lead to the oxidation of some of the minerals present in the tailings which then dissolve in water essentially resulting in its contamination. In a worst-case scenario, the sulfides that are common in tailings might react to produce sulfur dioxide gas or sulphuric acid which are toxic (MEND, 2006). Leaching essentially leads to the deterioration of the mining environment which can be catastrophic to the communities and the miners where mining is taking place.

Furthermore, leaching contributes to the weakening of the physical strength of the CPB thus making its efficacy in supporting underground mines poor (MEND, 2006). The adverse effects posed by leaching can, however, be mitigated during the design stages of the CPB. This can be done by instituting measures that slow the oxidation of the sulfides. Again, the design of the CPB should take into consideration the mechanical properties that are required to make the CPB durable by avoiding instances of possible cracking (MEND, 2006). The regulation of the porosity of the CPB impacts on its permeability which leads to controlled leaching and eventually contamination of the mining environment.

Experimental study by Bull and Fall (2020a,b) shed more light on the current understanding of the leachability of CPB with a focus on the influence of curing temperature and binder type. The leaching of arsenic, a metalloid that naturally coexist with many mined minerals, from CPB specimens containing PCI and/or blast furnace slag was monitored under curing temperatures of 2, 20, and 35 °C. The researchers conducted microstructural analyses to ascertain the changes in the hydrated cement matrix due to the factors being investigated and how that affects the leachability. The findings show that increasing the curing temperature decreases the performance of the CPB with regards to arsenic immobilization, ultimately decreasing the leachability. The reduction in leachability is attributed to the temperature-induced improvement of the pore structure of the CPB. High temperature accelerates binder hydration, whereby larger amounts of hydration products fill up the voids in the CPB. This limits the availability of arsenic for leaching and also makes the CPB less permeable. Similar behaviour was observed on the CPB containing both 100 percent PCI and CPB containing 50-50 PCI/Slag, although the former has better performance due to better binder hydration.

2.6.4 Hydraulic conductivity of CPB

Changes in hydraulic conductivity influences the effectiveness of the CPB (Chakilam and Cui, 2020). Sheshpari (2015) emphasizes the importance of designing CPB so that its drainage has the appropriate hydraulic conductivity to prevent retailing wall destruction and facilitate drainage. Similarly, Pokharel and Fall (2013) argue that temperature and sulphate significantly influence hydraulic conductivity and can either increase or decrease it. For instance, a decrease in temperature increases hydraulic conductivity (Jiang et al., 2017). As a result, it is critical to keep the temperature at an optimum level in order to avoid a negative impact on the CPB. Mathematical modeling can be incorporated into the backfill design to control the CPB's behavioral mechanisms as well as the associated influential factors (Cui and Fall, 2018c). Such measures help control the hydraulic conductivity.

According to Qi and Fourie (2019), CPB is a cost-effective and environmentally friendly technique of managing mineral tailings disposal. Therefore, it is critical to maintaining the proper working conditions, including the Hydraulic Conductivity of CPB, to increase its effectiveness. Jiang et al. (2017) assert that artificial intelligence can be used to improve CPB design. The results can then be interpreted using atomic simulation (Jiang et al., 2017). Jafari et al. (2021) present a CPB study conducted in the Williams mine in Ontario, Canada, demonstrating that a relatively high hydraulic conductivity is likely to cause shearing of the CPB under in-situ static conditions. As a result, the hydraulic conductivity of CPB must be kept at an appropriate level.

Fall et al. (2009) extensively studied the hydraulic conductivity of CPB and identified different factors that influence it. They also developed a model that predicts the hydraulic conductivity as a time dependent parameter. Flexible wall permeability test with a constant head was used. Factors that were investigated include curing time, binder content, binder type, tailings fineness, initial sulphate content, water to cement ratio, and curing temperature. The findings show that the hydraulic conductivity of CPB is generally time-dependent, decreasing the curing time increases. Other factors that have an inverse effect on the hydraulic conductivity are the binder content, tailings fineness, and curing temperature. Increase in the water to cement ratio, on the other hand, leads to the increase of the hydraulic conductivity. Initial sulphate was found to have two opposite effects on the hydraulic conductivity. At the early age, up to 28 days of curing, CPB containing sulphate has lower hydraulic conductivity due to low porosity caused by precipitation of secondary cement hydration products. At old curing age (90 days and above), the CPB containing high sulphate content become more permeable due to the development of microcracks as the amount of expansive hydration products become excessive.

2.7 Review of the literature on the use of superplasticizers in CPB

Superplasticizers were developed in the early 1960s (Hattori, 1979; Flatt and Schober, 2012) and became widely used in the production of concrete over the following decades. They have become indispensable in the production of high-strength and ultra-high-strength concrete (De Reese et al.,2013; Plank et al., 2015). For, this reason, there have been a plethora of scientific studies on their influence on concrete and other construction materials. Because CPB is a very recent innovation, which, unlike typical construction materials, uses toxic waste material (tailings), there is a limited research studies its properties (Yilmaz et al., 2014). There have been a number of studies, mostly in the past five years, aimed at understanding the effects of superplasticizers on various properties of CPB. The investigated properties can be grouped into i) rheology ii) mechanical strength.

2.7.1 Rheology

Significant part of the research on the use of superplasticizers in CPB is about their effects on rheological properties. This is unsurprising because the main purpose of these form of chemical admixtures is to improve flowability of cementitious materials. Thus, researchers would normally aim at understanding the applicability and efficiency of the superplasticizers in the backfill technology. Huynh et al. (2006) investigated the effects of two superplasticizers, polyphosphate-based and naphthalene sulphonate-based on the yield stress of dewatered tailings and fresh CPB. They also used depletion method to test the nature of adsorption of the two superplasticizers onto the tailings and cement particles. They found out that both polyphosphate and naphthalene sulphonate superplasticizers leads to the reduction of yield stress in both dewatered tailings and CPB mixture. However, the polyphosphate is more effective in reducing the yield stress of the tailings than that of the CPB. On the other hand, naphthalene sulphonate superplasticizers have commensurate reducing effect on the yield stresses of both materials. The reason for the differing activity of the two forms of superplasticizers is that cement hydration has a more pronounced negative influence on the dispersion effects of the polyphosphate.

Simon et al. (2011), Panchal et al. (2018), Outtara et al. (2017), and Outtara et al. (2018a) studied the rheological effects properties of CPB admixed with a polycarboxylic-based superplasticizers with yield stress and viscosity as the main parameters of interest. This type of superplasticizer causes dispersion by through adsorption of its long polymer-chain molecules by the cement particles based on a mechanism termed as steric hinderance (Panchal et al., 2018; Chuang et al., 2019). The tailings used in these studies have solid contents varying from 75% to 80% while the binder content varied from 3.5% to 6% of the total solids. Simon et al. (2011) observed up to 100% decrease in yield stress by adding a superplasticizer content of 0.3%. They also observed a setting time delay due to the incorporation of the superplasticizer. Panchal et al. (2011) observed 8% and 20% drops in the yield stress and apparent viscosity respectively upon increasing the superplasticizer content by 0.1%. They also observed a delay in the hydration process, which was linked to the reduction of Ca2+ ions responsible for the production of hydration products such as ettringite and CH. Finally, Outtara et al. (2017) discovered that varying the binder content in the CPB has a negligible impact on the effects of the polycarboxylic-based superplasticizers, which contrasts with the other types. Also, they give a 0.121% of the total mass of the CPB as the most effective superplasticizer content.

2.7.2 Mechanical strength

Due to the importance of mechanical stability in the design of backfills, there have been a number of studies that investigated the effects of superplasticizers on the UCS of CPB structures. Klein and Simon (2006) studied the effects of polycarboxylic-based and naphthalene sulphonate, and melamine sulphonate superplasticizers on the setting time and strength development of cemented paste backfill. The initial and final setting times were measured using a standard Vicat needle test. Unconfined compressive strength measurements were taken at 28, 182, and 365days. The findings revealed that melamine sulphonate superplasticizer has a significantly higher retardation effect on the setting time of the CPB than polycarboxylic-based superplasticizers. The retardation capability of the naphthalene sulphonate was observed to depend on the content of the sulphonic group polymer in the chemical admixture (higher content of sulphonic group increases the retardation capability). The effect of the superplasticizers on the UCS was also inconsistent. The naphthalene sulphonate only improves the UCS of CPB at the 28 days curing age but caused a decrease of about 20% and 25% at the 182 days and 365 days respectively. On the other hand, polycarboxylic-based superplasticizer was observed to significantly improve the UCS of the CPB at all ages, with an increase of about 80% at 365 days of curing. The improvement was largely associated with a better particle packing as well as denser material structure when this kind of superplasticizer is used.

Zheng et al. (2016) conducted an experimental study to investigate the coupled effects of naphthalene sulphonate superplasticizer and limestone powder on the compressive strength of CPB made of copper mine tailings with curing time varying from 1 to 112 days. As a pillar, adding 10% limestone powder to the CPB was found to improve the 28 days and 112 days UCS by 67% and 45% respectively. However, adding the superplasticizer significantly increase the percentages to 180% and 140% respectively. Incorporation of the two admixtures was credited with the alleviation of long-term loss of strength of CPB structures. Similarly, Yang et al. (2018) studied the coupled effects of solid contents and naphthalene sulphonate superplasticizer dosage on the UCS of CPB up to 28 days of curing. The researchers concluded that increasing the superplasticizer dosage leads to the increase of the UCS, especially at longer curing times (i.e., 7 days and 28 days).

Three separate research studies, namely Simon et al. (2011), Koohestani et al. (2018), and Outtara et al. (2018b), investigated the effects of polycarboxylic-based superplasticizers on the compressive strength of CPB. With the addition of 0.185% superplasticizer, Simon et al. (2011) recorded significant increase in UCS by about 130%, 70%, and 70% respectively at curing ages of 28, 182, and 365 days. Koohestani et al. (2018) used a superplasticizer content of 1% and curing times of 3, 7 and 28 days. Higher UCS values were recorded in each case, with increase of about 15%, 19%, and 54% respectively. Outtara et al. (2018b) used the superplasticizer contents of 0.09%, 0.121%, 0.135%, and 0.153%. Adding the superplasticizer immediately together with the mixing water increased the UCS by up to 25% after a curing time of 28 days. However, delaying the addition of superplasticizer by 3 minutes improved the UCS by up to 29%. Other studies on the use of superplasticizer supported the observed benefit of delaying its incorporation in the mixture (Hassani et al., 2001; Klein and Simon, 2006; El-Didamony et al., 2012).

Mangane et al. (2018) compared the performance of four different superplasticizer types (naphthalene sulphonate, polycarboxylic, lignosulphate, and melamine sulphonate) in terms of the compressive strength of CPB. The contents of the superplasticizers were also varied in order to identify the most effective percentages. For the lignosulphate, and melamine sulphonate, the optimal content was found to be 5% of the weight of binder. For the naphthalene sulphonate, polycarboxylic based superplasticizers, the optimal content is 7%. At these percentages, polycarboxylic based superplasticizer exhibited the highest improvement in the UCS values. At 7 days and 28 days, the UCS increased by about 180% and 120% respectively. The recorded improvements for the other superplasticizer types are: naphthalene sulphonate – 35% and 20%; lignosulphate – 20% and 40%; melamine sulphonate – 20% and 28%.

2.8 Conclusion

The CPB technology is an innovative and sustainable tailings management method as opposed to surface disposal. One of the challenges in the preparation and transportation of the CPB is achieving an adequate flowability without undermining its stability. To tackle this problem, superplasticizers, which improve the workability of the CPB without the need for increasing water content, are incorporated during the mixing process. It is evident from the published literature that superplasticizers are important in the production of CPB with sufficient flowability. All types of superplasticizers are shown to be effective in decreasing the yield stress and viscosity which are the typical parameters used in determining the transportability of the CPB. The content of the superplasticizer that is generally used vary from 0.1% to 1% of the total CPB mass. Beside the improvement of the flowability, the superplasticizer also has a tendency of delaying the setting time of the CPB mixture. Furthermore, the reviewed literature indicate that the chemical admixture generally improves the compressive strength of CPB structures. Polycarboxylic-based superplasticizers appeared to be the most effective in terms of strength improvement at both early and old age. The available literature on the use of superplasticizers in CPB is very limited, several other properties that are important to its overall performance are yet to be investigated.

In essence, the influence of superplasticizers on the geotechnical and environmental properties of the CPB is not fully understood. Based on the theoretical and technical background presented, it is clear that properties such as rheology, mechanical strength, reactivity, and hydraulic conductivity under different temperature conditions are essential for the effective performance of CPB systems. Therefore, investigation of these parameters would be the focus of this PhD research. Findings from the study will provide beneficial information for proper and sustainable design of CPB structures.

2.9 References

Agulló, L., Toralles-Carbonari, B., Gettu, R., & Aguado, A. (1999). Fluidity of cement pastes with mineral admixtures and superplasticizer—A study based on the Marsh cone test. *Materials and Structures*, 32(7), 479-485.

Aicha, M. B. (2020). The superplasticizer effect on the rheological and mechanical properties of self-compacting concrete. In *New Materials in Civil Engineering* (pp. 315-331). Butterworth-Heinemann.

Amaratunga, L. M., & Yaschyshyn, D. N. (1997). Development of a high modulus paste fill Using fine gold mill tailings. *Geotechnical & Geological Engineering*, *15*(3), 205-219.

ASTM C1494/C494M-17 (2017). Standard specification for chemical admixtures for concrete. West Conshohocken, PA: ASTM International.

Bhatty, J. I. (1991). A review of the application of thermal analysis to cement-admixture systems. *Thermochimica Acta*, *189*(2), 313-350.

Belem, T., & Benzaazoua, M. (2004). An overview on the use of paste backfill technology as a ground support method in cut-and-fill mines. In *Proceedings of the 5th Int. Symp. on Ground support in Mining and Underground Construction. Villaescusa & Potvin (eds.)* (pp. 28-30).

Belem, T., & Benzaazoua, M. (2008). Design and application of underground mine paste backfill technology. *Geotechnical and Geological Engineering*, *26*(2), 147-174.

Benaicha, M., Jalbaud, O., Alaoui, A. H., & Burtschell, Y. (2015). Marsh cone coupled to a plexiglas horizontal channel: Rheological characterization of cement grout. *Flow Measurement and Instrumentation*, *45*, 126-134.

Benzaazoua, M., Marion, P., Picquet, I., & Bussière, B. (2004). The use of pastefill as a solidification and stabilization process for the control of acid mine drainage. *Minerals engineering*, *17*(2), 233-243.

Bergold, S. T., Goetz-Neunhoeffer, F., & Neubauer, J. (2017). Interaction of silicate and aluminate reaction in a synthetic cement system: Implications for the process of alite hydration. *Cement and Concrete Research*, *93*, 32-44.

Blowes, D. W., Ptacek, C. J., Jambor, J. L., & Weisener, C. G. (2003). The geochemistry of acid mine drainage. Chapter 9.05 of the Treatise on geochemistry, Rolland, HD and Turekian, KK.

Bull, A. & Fall, M. (2020a). Curing temperature dependency of the release of Arsenic from cemented paste backfill made with Portland cement. *Journal of Environmental Management 269*: 110772.

Bull, A. J., & Fall, M. (2020b). Thermally induced changes in metalloid leachability of cemented paste backfill that contains blast furnace slag. *Minerals Engineering*, *156*, 106520.

Cao, S., Yilmaz, E., & Song, W. (2018). Evaluation of viscosity, strength and microstructural properties of cemented tailings backfill. *Minerals*, *8*(8), 352.

Cayouette J (2003) Optimization of the paste backfill plant at Louvicourt mine. CIM Bull 96(1075):51–57

Célestin, J. & Fall, M. (2009). Thermal conductivity of cemented paste backfill material and factors affecting it. *International Journal of Mining, Reclamation And Environment*, 23(4), 274-290.

Chakilam, S., & Cui, L. (2020). Effect of polypropylene fiber content and fiber length on the saturated hydraulic conductivity of hydrating cemented paste backfill. *Construction and Building Materials*, *262*, 120854.

Cheng, H., Wu, S., Li, H., & Zhang, X. (2020). Influence of time and temperature on rheology and flow performance of cemented paste backfill. *Construction and Building Materials, 231*, 117117.

Cheng, H. Y., Wu, S. C., Zhang, X. Q., & Wu, A. X. (2020). Effect of particle gradation characteristics on yield stress of cemented paste backfill. *International Journal of Minerals, Metallurgy and Materials*, *27*(1), 10-17.

Chuang, P. H., Tseng, Y. H., Fang, Y., Gui, M., Ma, X., & Luo, J. (2019). Effect of side chain length on polycarboxylate superplasticizer in aqueous solution: A computational study. *Polymers*, *11*(2), 346.

Cihangir, F., Kesimal, A., Deveci, H., & Alp, Ì. (2010). Effect of natural pozzolans as mineral admixture on the performance of cemented-paste backfill of sulphide-rich tailings. *Waste Management & Research*, 28(5), 430-435.

Cooke, R. (2001). Design procedure for hydraulic backfill distribution systems. *Journal of the Southern African Institute of Mining and Metallurgy*, *101*(2), 97-102.

Coussot, P. (2014). Yield stress fluid flows: A review of experimental data. *Journal of Non Newtonian Fluid Mechanics*, *211*, 31-49.

Cui, L. & Fall, M., (2018a). Modeling of self-desiccation processes in cemented tailings backfill structures. I*nternational Journal for Numerical and Analytical Methods in Geomechanics* 42,558-583.

Cui, L. & Fall, M., (2018b). Multiphysics modeling and simulation of strength development and distribution in cemented tailings backfill structures. *International Journal of Concrete Structures and Materials 12* (1), 1-22.

Cui, L. & Fall, M., (2018c). Mathematical modeling of cemented tailings backfill: a review. *International Journal of Mining, Reclamation and Environment 33 (6)*, 389-408.

Cyr, M., Legrand, C., & Mouret, M. (2000). Study of the shear thickening effect of superplasticizers on the rheological behaviour of cement pastes containing or not mineral additives. *Cement and Concrete Research*, 30(9), 1477-1483.

de ARAÚJO, E. E. B., Simon, D., de FRANÇA, F. A. N., & de Freitas Neto, O. (2017). Shear strength of a cemented paste backfill submitted to high confining pressure. In *Applied Mechanics and Materials* (Vol. 858, pp. 219-224). Trans Tech Publications Ltd.

Darweesh, H. H. M. (2016). Black liquor waste as a cement admixture or cement and concrete admixtures. In *Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials* (pp. 99-130). Woodhead Publishing.

Deng, X. J., Klein, B., Hallbom, D. J., de Wit, B., & Zhang, J. X. (2018). Influence of particle size on the basic and time-dependent rheological behaviors of cemented paste backfill. *Journal of Materials Engineering and Performance*, *27*(7), 3478-3487.

De Kee, D. (2021). Yield stress measurement techniques: A review. *Physics of Fluids*, 33(11), 111301.

De Reese, J., Lenz, P., Zilch, K., & Plank, J. (2013). Influence of type of superplasticizer and cement composition on the adhesive bonding between aged and fresh concrete. *Construction and Building Materials*, *48*, 717-724.

Deschamps, T., Benzaazoua, M., Bussière, B., Aubertin, M., & Belem, T. (2008). Microstructural and geochemical evolution of paste tailings in surface disposal conditions. *Minerals Engineering*, 21(4), 341-353.

De Souza, E., Archibald, J., & Dirige, A. (2003). Economics and perspectives of underground backfill practices in Canadian mining. In *105th Annual General Meeting of the Canadian Institute of Mining, Metallurgy and Petroleum. Montreal*.

Donovan, J. G. (1999). *The effects of backfilling on ground control and recovery in thin-seam* *coal mining* (Doctoral dissertation, Virginia Polytechnic Institute and State University).

Druschel, G. K., Baker, B. J., Gihring, T. M., & Banfield, J. F. (2004). Acid mine drainage biogeochemistry at Iron Mountain, California. *Geochemical Transactions*, *5*(2), 1-20.

Dutta, M., Islam, N. & Rabha, S. (2020). Acid mine drainage in an Indian high-sulfur coal mining area: Cytotoxicity assay and remediation study. Journal of Hazardous Materials, *389*, 121851, ISSN 0304-3894.

Edmeades, R. M., & Hewlett, P. C. (1998). Cement admixtures. In *Lea's chemistry of cement and concrete* (pp. 841-905). Butterworth-Heinemann.

El-Didamony, H., Heikal, M., Khalil, K. A., & Al-Masry, S. (2012). Effect of delaying addition time of SMF superplasticizer on the physico-mechanical properties and durability of cement pastes. *Construction and Building Materials*, *35*, 261-269.

Ercikdi, B., Cihangir, F., Kesimal, A., Deveci, H., & Alp, İ. (2010). Utilization of water-reducing admixtures in cemented paste backfill of sulphide-rich mill tailings. *Journal of Hazardous Materials*, 179(1-3), 940-946.

Fall, M., Benzaazoua, M., & Ouellet, S. (2005). Experimental characterization of the influence of tailings fineness and density on the quality of cemented paste backfill. *Minerals Engineering*, *18*(1), 41-44.

Fall, M., Benzaazoua, M., & Saa, E. (2008). Mix proportioning of underground cemented tailings backfill. *Tunnelling and Underground Space Technology*, 23(1), 80-90.

Fall, M., Adrien, D., Célestin, J. C., Pokharel, M., & Touré, M. (2009). Saturated hydraulic conductivity of cemented paste backfill. *Minerals Engineering*, *22*(15), 1307-1317.

Fang, K. & Fall, M. (2019). Chemically induced changes in shear behaviour of interface between rock and tailings backfill undergoing cementation. *Rock Mechanics and Rock Engineering* *2 (*9), 3047-3062.

Fang, K., Cui, L. & Fall, M. (2020). A coupled chemo-elastic cohesive zone model for backfill-rock interface. Computer & Geotechnics 125: 103666.

Ferraris, C., Obla, K., & Hill, R. (2001). The influence of mineral admixtures on the rheology of cement paste and concrete. *Cement and Concrete Research*, 31(2), 245-255.

Flatt, R., & Schober, I. (2012). Superplasticizers and the rheology of concrete. In *Understanding the rheology of concrete* (pp. 144-208). Woodhead publishing.

Fu, J., Song, W., & Tan, Y. (2016). Study on Microstructural Evolution and Strength Growth and Fracture Mechanism of Cemented Paste Backfill. Advances In Materials Science And Engineering, 2016, 1-13.

Gagne, R. (2016). Shrinkage-reducing admixtures. *Science and Technology of Concrete Admixtures*, *457-469*

Gelardi, G., Mantellato, S., Marchon, D., Palacios, M., Eberhardt, A. B., & Flatt, R. J. (2016). Chemistry of chemical admixtures. In *Science and technology of concrete admixtures* (pp. 149-218). Woodhead Publishing.

Haiqiang, J., Fall, M., & Cui, L. (2016). Yield stress of cemented paste backfill in sub-zero environments: experimental results. *Minerals Engineering*, *92*, 141-150.

Hamberg, R., Maurice, C., & Alakangas, L. (2015). The use of low binder proportions in cemented paste backfill–effects on As-leaching. Minerals Engineering, 78, 74-82.

Hassani, F. P., Ouellet, J., & Hossein, M. (2001). Strength development in underground high sulphate paste backfill operation. *CIM bulletin*, *94*.

Hattori, K. (1979). Experiences with Mighty superplasticizer in Japan. *Special Publication*, *62*, 3766.

Huntzinger, D. N., & Eatmon, T. D. (2009). A life-cycle assessment of Portland cement manufacturing: comparing the traditional process with alternative technologies. Journal of Cleaner Production, 17(7), 668-675.

Huynh, L., Beattie, D. A., Fornasiero, D., & Ralston, J. (2006). Effect of polyphosphate and naphthalene sulfonate formaldehyde condensate on the rheological properties of dewatered tailings and cemented paste backfill. *Minerals Engineering*, *19*(1), 28-36.

Ichrak, H., Mostafa, B., Abdelkabir, M., & Bruno, B. (2016). Effect of cementitious amendment on the hydrogeological behavior of a surface paste tailings' disposal. *Innovative Infrastructure Solutions*, 1(1).

Igarashi, T., Herrera, P. & Uchiyama, H. (2020). The two-step neutralization ferrite-formation process for sustainable acid mine drainage treatment: Removal of copper, zinc and arsenic, and the influence of coexisting ions on ferritization. *Science of The Total Environment, 715*, 136877, ISSN 0048-9697.

Jacobs, J. A., & Testa, S. M. (2014). Acid Drainage and Sulfide Oxidation: Introduction. *Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, Prediction, Prevention, and Remediation*, 3.

Jafari, M., Shahsavari, M., & Grabinsky, M. (2021). Drained triaxial compressive shear response of cemented paste backfill (CPB). *Rock Mechanics and Rock Engineering*, *54*(6), 3309-3325.

Jennings, S. R., Blicker, P. S., & Neuman, D. R. (2008). *Acid mine drainage and effects on fish health and ecology: a review*. Reclamation Research Group.

Jiang, H. & Fall, M. (2017). Yield stress and strength of saline cemented tailings materials in sub-zero environments: slag-paste backfill. *Journal of Sustainable Cement-Based Materials*, 1-18.

Jiang, H., Fall, M., & Cui, L. (2017). Freezing behaviour of cemented paste backfill material in column experiments. *Construction and Building Materials*, *147*, 837-846.

Jiang, H., Fall, M., Yilmaz, E., Li, Y., & Yang, L. (2020). Effect of mineral admixtures on flow properties of fresh cemented paste backfill: Assessment of time dependency and thixotropy. *Powder Technology*, *372*, 258-266.

Jung, S. J., & Biswas, K. (2002). Review of current high density paste fill and its technology. *Mineral Resources Engineering*, *11*(02), 165-182.

Karfakis, M. G., Bowman, C. H., & Topuz, E. (1996). Characterization of coal-mine refuse as backfilling material. *Geotechnical & Geological Engineering*, *14*(2), 129-150.

Kefeni, K., Msagati, t. & Mamba, B. (2017). Acid mine drainage: Prevention, treatment options, and resource recovery: A review. *Journal of Cleaner Production*, *151*: 475-493, ISSN 0959-6526.

Kesimal, A., Yilmaz, E., Ercikdi, B., Alp, I., & Deveci, H. (2005). Effect of properties of tailings and binder on the short-and long-term strength and stability of cemented paste backfill. *Materials Letters*, *59*(28), 3703-3709.

Khan, S., Nuruddin, M., Ayub, T., & Shafiq, N. (2014). Effects of Different Mineral Admixtures on the Properties of Fresh Concrete. *The Scientific World Journal*, 2014, 1-11.

Klein, K., & Simon, D. (2006). Effect of specimen composition on the strength development in cemented paste backfill. *Canadian Geotechnical Journal*, *43*(3), 310-324.

Komurlu, E., Cihangir, F., Turan, A., Kesimal, A., & Ercikdi, B. (2017). An Experimental Study on Shear Strength of Cemented Paste Backfill Materials. *Süleyman Demirel Üniversitesi Fen Bilimleri Enstitüsü Dergisi*, *22*(1), 45-52.

Koohestani, B., Darban, A. K., & Mokhtari, P. (2018). A comparison between the influence of superplasticizer and organosilanes on different properties of cemented paste backfill. *Construction and Building Materials*, *173*, 180-188.

Kou, Y., Jiang, H., Ren, L., Yilmaz, E., & Li, Y. (2020). Rheological properties of cemented paste backfill with alkali-activated slag. *Minerals*, *10*(3), 288.

Koupouli, N., Belem, T., Rivard, P., & Effenguet, H. (2016). Direct shear tests on cemented paste backfill–rock wall and cemented paste backfill–backfill interfaces. Journal of Rock *Mechanics and Geotechnical Engineering*, 8(4), 472-479.

Külekçi, G., Erçikdi, B., & Aliyazicioğlu, Ş. (2016, October). Effect of Waste Brick as Mineral Admixture on the Mechanical Performance of Cemented Paste Backfill. In *IOP Conference Series: Earth and Environmental Science* (Vol. 44, No. 4, p. 042039). IOP Publishing.

Larson, R. G. (1999). *The structure and rheology of complex fluids* (Vol. 150). New York: Oxford university press.

Larsson, M., Duffy, J., & AB, M. (2013). An overview of measurement techniques for determination of yield stress. *Annu. Trans. Nordic Rheol. Soc*, *21*, 125-138.

Iatan, E. L. (2021). Gold mining industry influence on the environment and possible phytoremediation applications. In *Phytorestoration of Abandoned Mining and Oil Drilling Sites* (pp. 373-408). Elsevier.

Lindsay, M. B., Moncur, M. C., Bain, J. G., Jambor, J. L., Ptacek, C. J., & Blowes, D. W. (2015). Geochemical and mineralogical aspects of sulfide mine tailings. Applied geochemistry, 57, 157-177.

Lingga, B. A., & Apel, D. B. (2018). Shear properties of cemented rockfills. *Journal of Rock Mechanics and Geotechnical Engineering*, *10*(4), 635-644.

Lottermoser, B. G. (2010). Sulfidic mine wastes. In *Mine wastes* (pp. 43-117). Springer, Berlin, Heidelberg.

Lu, S. H., Liu, G., Ma, Y. F., & Li, F. (2010). Synthesis and application of a new vinyl copolymer superplasticizer. *Journal of Applied Polymer Science*, *117*(1), 273-280.

Ma, Y., Dickinson, N., & Wong, M. (2002). Toxicity of Pb/Zn mine tailings to the earthworm Pheretima and the effects of burrowing on metal availability. *Biology and Fertility of Soils*, *36*(1), 79-86.

Mangane, M. B. C., Argane, R., Trauchessec, R., Lecomte, A., & Benzaazoua, M. (2018). Influence of superplasticizers on mechanical properties and workability of cemented paste backfill. *Minerals Engineering*, *116*, 3-14.

MEND (2006). Paste Backfill Geochemistry - Environmental Effects of Leaching and Weathering. http://mend-nedem.org. Web: March, 9 2017, Retrieved from http://mend-nedem.org/wp-content/uploads/2013/01/10.2.pdf

Mbugua, R., Salim, R., & Ndambuki, J. (2016). Effect of Gum Arabic Karroo as a water reducing admixture in cement mortar. *Case Studies in Construction Materials*, *5*, 100-111.

Naidu, G., Ryu, S. & Thiruvenkatachari et. al. (2019). A critical review on remediation, reuse, and resource recovery from acid mine drainage, *Environmental Pollution, 247*: 1110-1124, ISSN 0269-7491.

Neto, E., Magina, S., Camões, A., Begonha, A., Evtuguin, D. V., & Cachim, P. (2016). Characterization of concrete surface in relation to graffiti protection coatings. *Construction and Building Materials*, *102*, 435-444.

Niroshan, N., Sivakugan, N., & Veenstra, R. L. (2018). Flow characteristics of cemented paste backfill. *Geotechnical and Geological Engineering*, *36*(4), 2261-2272.

Nkinamubanzi, P. C., Mantellato, S., & Flatt, R. J. (2016). Superplasticizers in practice. In *Science and technology of concrete admixtures* (pp. 353-377). Woodhead Publishing.

Panchal, S., Deb, D., & Sreenivas, T. (2018). Variability in rheology of cemented paste backfill with hydration age, binder and superplasticizer dosages. *Advanced Powder Technology*, *29*(9), 2211-2220.

Partal, P., & Franco, J. M. (2010). Non-newtonian fluids. *Rheology: encyclopaedia of life support systems (EOLSS), UNESCO. Eolss, Oxford*, 96-119.

Ouattara, D., Yahia, A., Mbonimpa, M., & Belem, T. (2017). Effects of superplasticizer on rheological properties of cemented paste backfills. *International Journal of Mineral Processing*, *161*, 28-40.

Ouattara, D., Mbonimpa, M., Yahia, A., & Belem, T. (2018a). Assessment of rheological parameters of high density cemented paste backfill mixtures incorporating superplasticizers. *Construction and Building Materials*, *190*, 294-307.

Ouattara, D., Belem, T., Mbonimpa, M., & Yahia, A. (2018b). Effect of superplasticizers on the consistency and unconfined compressive strength of cemented paste backfills. *Construction and Building Materials*, *181*, 59-72.

Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals engineering*, *19*(5), 407-419.

Panchal, S., Deb, D., & Sreenivas, T. (2018). Variability in rheology of cemented paste backfill with hydration age, binder and superplasticizer dosages. *Advanced Powder Technology*, *29*(9), 2211-2220.

Park, I., Tabelin, C., & Jeon, S. et. al. (2018). A review of recent strategies for acid mine drainage prevention and mine tailings recycling, Chemosphere, *219*: 588-606, ISSN 0045-6535.

Plank, J., Sakai, E., Miao, C. W., Yu, C., & Hong, J. X. (2015). Chemical admixtures

Chemistry, applications and their impact on concrete microstructure and durability. *Cement and concrete research*, *78*, 81-99.

Pokharel, M., & Fall, M. (2010). Coupled thermochemical effects on the strength development of slag-paste backfill materials. *Journal of Materials in Civil Engineering*, *23*(5), 511-525.

Pokharel, M., & Fall, M. (2013). Combined influence of sulphate and temperature on the saturated hydraulic conductivity of hardened cemented paste backfill. *Cement and Concrete Composites*, *38*, 21-28.

Qi, C., Chen, Q., Fourie, A., & Zhang, Q. (2018). An intelligent modelling framework for mechanical properties of cemented paste backfill. *Minerals Engineering*, *123*, 16-27.

Qi, C., & Fourie, A. (2019). Cemented paste backfill for mineral tailings management: Review and future perspectives. *Minerals Engineering*, *144*, 106025.

Qian, Y., Lesage, K., El Cheikh, K., & De Schutter, G. (2018). Effect of polycarboxylate ether superplasticizer (PCE) on dynamic yield stress, thixotropy and flocculation state of fresh cement pastes in consideration of the Critical Micelle Concentration (CMC). *Cement and Concrete Research*, *107*, 75-84.

Rambabu, K., Banat, F., & Pham, Q. et. al. (2020). Biological remediation of acid mine drainage: Review of past trends and current outlook. *Environmental Science and Ecotechnology, 2*, 100024. ISSN 2666-4984.

Rankine, R. M., & Sivakugan, N. (2007). Geotechnical properties of cemented paste backfill from Cannington Mine, Australia. *Geotechnical and Geological Engineering*, *25*(4), 383-393.

Reid, C., Becaert, V., Aubertin, M., Rosenbaum, R. K., & Deschênes, L. (2009). Life cycle assessment of mine tailings management in Canada. *Journal of Cleaner Production, 17*(4), 471-479.

Rezaie, B. & Anderson, A. (2020). Sustainable resolutions for environmental threat of the acid mine drainage. *Science of The Total Environment*, *717*:137211, ISSN 0048-9697.

Roncero, J., Valls, S., & Gettu, R. (2002). Study of the influence of superplasticizers on the hydration of cement paste using nuclear magnetic resonance and X-ray diffraction techniques. *Cement and Concrete Research*, *32*(1), 103-108.

Roshani, A., & Fall, M. (2020). Rheological properties of cemented paste backfill with nano-silica: link to curing temperature. *Concrete and Cement Composites 114*, 103785.

Sasaki, K., Tsunekawa, M., Ohtsuka, T., & Konno, H. (1995). Confirmation of a sulfur-rich layer on pyrite after oxidative dissolution by Fe (lIl) ions around pH2. *Geochimica et Cosmochimica Acta*, *59*(15), 3155-3158.

Sheshpari, M. (2015). A review of underground mine backfilling methods with emphasis on cemented paste backfill. *Electron J Geotech Eng*, *20*, 5183-5208.

Simon, D., Grabinsky, M. W., & Bawden, W. (2011, October). Effect of polycarboxylated acrylic acid polymer-based superplasticizer on cemented paste backfill. In *Proceedings of the Canadian Geotechnical Conference, Toronto, ON, Canada* (pp. 2-6).

Sivakugan, N., Rankine, K., & Rankine, R. (2006). Permeability of hydraulic fills and barricade bricks. *Geotechnical & Geological Engineering*, *24*(3), 661-673.

Skousen, J., Ziemkiewicz, P., & McDonald, L. (2019). Acid mine drainage formation, control and treatment: Approaches and strategies. *The Extractive Industries and Society, 6*(1): 241-249.

Stengel, T., & Schießl, P. (2014). Life cycle assessment (LCA) of ultra high performance concrete

(UHPC) structures. In *Eco-efficient Construction and Building Materials* (pp. 528-564). Woodhead Publishing.

Stone, D. (2014, May). The evolution of paste for backfill. In *Mine Fill 2014: Proceedings of the Eleventh International Symposium on Mining with Backfill* (pp. 31-38). Australian Centre for Geomechanics.

Tkach, E. V., Semenov, V. S., Tkach, S. A., & Rozovskaya, T. A. (2015). Highly effective water-repellent concrete with improved physical and technical properties. *Procedia Engineering*, *111*, 763-769.

Tomiyama, S., Igarashi, T., Tabelin, C. B., Tangviroon, P., & Ii, H. (2019). Acid mine drainage sources and hydrogeochemistry at the Yatani mine, Yamagata, Japan: A geochemical and isotopic study. *Journal of contaminant hydrology*, *225*, 103502.

Thompson, B. D., Bawden, W. F., & Grabinsky, M. W. (2012). In situ measurements of Cemented paste backfill at the Cayeli Mine. *Canadian Geotechnical Journal*, *49*(7), 755-772.

Van Oss, H. G., & Padovani, A. C. (2002). Cement manufacture and the environment: part I: chemistry and technology. *Journal of Industrial Ecology*, *6*(1), 89-105.

Vick, S. G. (1984). A systematic approach to tailings impoundment siting. *Mining Science and Technology*, *1*(4), 285-297.

Wang, C., Harbottle, D., Liu, Q., & Xu, Z. (2014). Current state of fine mineral tailings treatment: A critical review on theory and practice. *Minerals Engineering*, *58*, 113-131.

Wang, H., Yang, L., Li, H., Zhou, X., & Wang, X. (2019). Using coupled rheometer-FBRM to study rheological properties and microstructure of cemented Paste Backfill. *Advances in Materials Science and Engineering*, *2019*.

Wong, I. Y. H., & Wong, D. S. H. (2013). Special adjuncts to treatment. *Retina (5th ed.)*.

Wu, D., & Cai, S. J. (2015). Coupled effect of cement hydration and temperature on hydraulic behavior of cemented tailings backfill. *Journal of Central South University*, *22*(5), 1956-1964.

Wu, A. X., Ruan, Z. E., Wang, Y. M., Yin, S. H., Wang, S. Y., Wang, Y., & Wang, J. D. (2018). Simulation of long-distance pipeline transportation properties of whole tailings paste with high sliming. *Journal of Central South University*, *25*(1), 141-150.

Xu, R., Li, B., Xiao, E., Young, L. Y., Sun, X., Kong, T., ... & Sun, W. (2020). Uncovering microbial responses to sharp geochemical gradients in a terrace contaminated by acid mine drainage. *Environmental Pollution*, *261*, 114226.

Yan, B., Ren, F., Cai, M., & Qiao, C. (2019). Influence of new hydrophobic agent on the mechanical properties of modified cemented paste backfill. *Journal of Materials Research and Technology*, *8*(6), 5716-5727.

Yilmaz, E., Benzaazoua, M., Belem, T., & Bussière, B. (2009). Effect of curing under pressure on compressive strength development of cemented paste backfill. *Minerals Engineering*, *22*(9), 772-785.

Yilmaz, E., Belem, T., & Benzaazoua, M. (2014). Effects of curing and stress conditions on hydromechanical, geotechnical and geochemical properties of cemented paste backfill. *Engineering Geology*, *168*, 23-37.

Yılmaz, T., Ercikdi, B., & Deveci, H. (2018). Utilisation of construction and demolition waste as cemented paste backfill material for underground mine openings. *Journal of environmental management*, *222*, 250-259.

Yin, S., Wu, A., Hu, K., Wang, Y., & Zhang, Y. (2012). The effect of solid components on the rheological and mechanical properties of cemented paste backfill. *Minerals Engineering*, *35*, 61-66.

Zhang, C., Fu, J., Song, W., Kang, M., Li, T., & Wang, N. (2022). Analysis on mechanical behavior and failure characteristics of layered cemented paste backfill (LCPB) under triaxial compression. *Construction and Building Materials*, *324*, 126631.

Zhang, H. T., Feng, Q. X., Liu, C. L., Ren, X. Y., Yang, H. J., & Lin, S. D. (2021). Low-cost synthesis of high-performance polycarboxylic ether by Co2+-, Ni2+-and Zn2+-catalyzed H2O2-NaHSO3 initiation system. *Chemical Papers*, *75*(7), 3421-3428.

Zhang, M. H., Sisomphon, K., Ng, T. S., & Sun, D. J. (2010). Effect of superplasticizers on workability retention and initial setting time of cement pastes. *Construction and Building Materials*, *24*(9), 1700-1707.

Zhang, J., Zhang, Q., Sun, Q., Gao, R., Germain, D., & Abro, S. (2015). Surface subsidence control theory and application to backfill coal mining technology. *Environmental Earth Sciences*, *74*(2), 1439-1448.

Zhang, Q. L., Li, Y. T., Chen, Q. S., Liu, Y. K., Feng, Y., & Wang, D. L. (2021). Effects of temperatures and pH values on rheological properties of cemented paste backfill. *Journal of Central South University*, *28*(6), 1707-1723.

Zheng, J., Zhu, Y., & Zhao, Z. (2016). Utilization of limestone powder and water-reducing admixture in cemented paste backfill of coarse copper mine tailings. *Construction and Building materials*, *124*, 31-36.

Chapter 3. Technical paper I - Time- and temperature-dependent rheological properties of cemented paste backfill that contains superplasticizer

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Abstract

The use of suitable superplasticizers in the production of cemented paste backfill (CPB), a mix of water, binder and tailings particles, is becoming prevalent due to their ability to improve flowability without undermining other important engineering properties. Their performance under different ambient temperatures found in various regions is not well understood. No research has been conducted to understand the effects of temperature on the rheological properties of CPB with superplasticizers. Therefore, the aim of this study is to investigate the effects of a superplasticizer on the rheological properties, specifically yield stress and viscosity, of CPB prepared and cured under different temperatures. CPB mixes containing 0%, 0.05%, 0.125%, and 0.25% Master Glenium superplasticizer were prepared, and cured for 4 h at three different temperatures of 2 °C, 20 °C and, 35 °C. Yield stress and viscosity were determined at different time intervals over the period. Additional tests, such as pH, thermal analysis and zeta potential analysis were also conducted. It was found that an increase in the ambient temperature leads to higher yield stress and viscosity of CPB treated with superplasticizer. However, less amount of superplasticizer is required to maintain a sufficiently fluid CPB within few hours of production. Additionally, the results from the study showed that different dosages of the superplasticizer are required for different tailings types to achieve the same level of flowability. The findings of this study will be beneficial in the design and production of CPB material.

Keywords: Cemented paste backfill; Tailings; Superplasticizer; Temperature; Rheology; Mine.

3.1. Introduction

The use of Cemented Paste Backfill (CPB) has become mainstream in the mining industry (Liu et al. 2016) and since its introduction, many studies have been undertaken on the improvement of its production and performance. It is used for backfilling of mine stopes to provide ground support. This practice provides a safe environment for the miners, reduces mining cycles, and enhances the speed of mineral ore recovery (Ercridi, Kulekci & Yilmaz, 2017; Yilmaz 2016; Ouellet, Bussiere, Aubertin & Benzaazou, 2007; Jiang, Fall & Cui, 2017). Moreover, the negative environmental impact of tailings, which often contain hazardous compounds, is minimized by the CPB technology by safely storing it underground. CPB is basically a cementitious material made up of dewatered tailings with 70–85% solids, a hydraulic binder, and water (Fall et al., 2008; Wu et al., 2015).

The flowability of a mixed CPB is important during transportation from the surface, where the mixing plant is often located, to the underground mine stopes. The delivery is achieved either with the help of pumps and/or by gravity. Efficiency in this process is significant because any clogging as a result of insufficient fluidity results in operational delay and maintenance cost (Jung & Biswas, 2002; Wu et al. 2013). Water reducing admixtures (WRAs) are largely used in concrete production to improve flow while maintaining a minimal amount of mixing water without negatively affecting strength gain (Sahmaran, et al., 2006). The traditional WRAs, also referred to as plasticizers, have the capability of reducing the mixing water by 5–12% (ASTM C494, 2017; Barabanschikov and Komarinskiy, 2014). Superplasticizers are the high range WRAs that are capable of reducing the water content by 12–30% while maintaining desirable consistency and workability (Shi et al., 2016; Bravo et al., 2017). The most common superplasticizers used are either based on lignosulfonate or polycarboxylic compounds (Collepardi, 1998; Bravo et al., 2017). The lignosulfonate-based superplasticizers, which have the less water-reduction ability, operate based on electrostatic repulsion whereby the negatively charged ions from their molecules are adsorbed to the surface of the solid particles of the material being treated (Bravo et al., 2017). This hinders flocculation and provides a better pathway for the mixing water (Bravo et al., 2017). On the other hand, the polycarboxylic-based superplasticizers cause dispersion of particles based partly on the electrostatic repulsion (from the negatively charged carboxylic group) and largely on a mechanism called steric hindrance (Yoshioka et al., 1997; Pereira et al., 2012). The steric hindrance is characterized by a structure of the long poly-oxyethylene side chains in the chemical compound (Duan et al., 2013). The main chain attaches itself to the solid particles and hiders flocculation based on Pauli-Born repulsion (Bravo et al., 2017).

Various studies have been carried out recently with the aim of exploring the possibility of using such superplasticizers in the CPB technology. Ercikdi et al. (2010) investigated the effect of three different superplasticizers on the rheological and mechanical properties of CPB produced from sulphide-rich tailings. It was found out that admixtures containing polycarboxylate compounds improve the performance of CPB. In another study, the effects of polymeric dispersants on the flowability of CPB was investigated with a focus on the yield stress (Huynh et al. 2006). The admixtures were found to reduce the yield stress of the CPB by increasing the electrostatic repulsive force between particles. Another aspect of their application that has not yet been explored is their performance on CPB under different temperatures, although CPB is subjected in the field to various thermal loadings. Multiple studies with similar objective have been conducted on fresh concrete and cement mortars (e.g. Jolicoeur et al., 1997; Nawa et al., 2000; Ghapoori and Diawara, 2010; Kong and Sanjayan, 2010). Indeed, the study of commercial admixtures under varying conditions is essential for a better understanding of their applicability and efficiency. Studies on the effect of temperature on the rheological properties of CPB focused only on CPB materials that don't contain superplasticizer (Wu et al., 2013; Haiqiang et al., 2016; Wang et al., 2018). These studies show that the temperature can significantly affect the yield stress and apparent viscosity of CPB. However, to date, no studies have been conducted on the coupled effect of temperature and superplasticizer on the rheological properties of CPB. There is a need to address this research gap.

The main objective of this paper is, therefore, to present experimental results on the influence of mixing and curing temperature on the rheological properties of CPB containing superplasticizer. Two important parameters used for measuring the flowability of CPB are the viscosity and the yield stress.

3.2. Experimental Program

3.2.1 Materials used

CPB specimens containing different proportions of tailings, binders, water, and the chemical admixture (superplasticizer) were prepared for laboratory tests as outlined in this section.

3.2.1.1 Tailings

The mineralogical composition of the tailings used in CPB production influences the flow and strength characteristics of the CPB (Fall et al., 2010). Therefore, using different varieties of tailings would give results upon which conclusions can be drawn applicable to a wide range of tailings. For this study, three different types of tailings were used, namely artificial silica tailings (ST), as well as two natural tailings from Lake Shore Gold (LSG) and Tailings Ponds (TP). Constituting about 99.8% quartz by weight, ST is a non-reactive silica powder that minimizes uncertainties in the CPB properties caused by reactive elements (e.g., sulphides). With the natural tailings, such elements can interact with the binder, thereby affecting the interpretation of the results obtained (Fall et al., 2010). The mineral compositions of the tailings determined using X-Ray diffraction analysis are given in Table 3.1, whereas the physical properties of the tailings are given in Table 3.1. Unlike the ST, quartz makes up only about a quarter proportion in both natural tailings, with other important minerals such as albite, chlorite, and muscovite having a significant presence (Table 3.2). The main chemical compositions of the pore water of the natural tailings are shown in Table 3.3. Both natural tailings contain sulphate ions in their pore water.

Table 3.1. Physical properties of the tailings

Property	G_s	D_{10}	D_{30}	D_{50}	D_{60}	D_{90}	% fine	C_u	C_c	S_s
Unit	-	μm	μm	μm	μm	μm	(<2μm)			Cm^2/g
ST	2.70	1.9	9.0	22.5	22.5	88.9	90.0	16.6	1.3	3600
LSG	2.87	1.2	10.0	24	35.0	250.0	86.0	29.2	2.4	1819
TP	2.78	1.3	7.0	19.0	30.0	280.0	85.0	23.4	1.3	2491

Table 3.2. Mineral compositions of the tailings

Tailings/Mineral (wt.%)	Quartz	Albite	K feldspar	Chlorite	Muscovite	Biotite	Dolomite	Calcite	Sepiolite	Apatite	Others	Total
ST	99.8										0.2	100
LSG	22.5	18.6	3.8	11.7	8.1	2.6	23.3	4.1	2.5	2.4	0.4	100
TP	26.1	21.3	-	11.4	26.3	2.7	11.3	-	-	-	0.9	100

Table 3.3. Pore water chemistry of the natural tailings

Tailings/ion (ppm)	Al	K	As	Ca	Si	Ni	Cu	Fe	Mg	Co	Mn	Sr	Na	S	So_4^{2-}
LSG	<1	107	<300	466	3.3	95	<20	0.16	696	80	2.75	7190	267	1420	4210
TP	<1	25.8	<300	455	1.8	448	<20	0.29	1130	264	3.93	1690	48.9	1770	5270

3.2.1.2. Binder and water

Portland cement type I (PCI) was used as the sole binder for all the CPB samples used in this study. PCI is the most frequent type of binder used in CPB technology. Tap water was used for mixing the binder and tailings.

3.2.1.3. Chemical admixture

Master Glenium 7500 (Master G), a product of the chemical company, Badische Andilin und Soda Fabrik (BASF), was used as the superplasticizer in the CPB mix. It is a full range water reducing admixture generally used for workability improvements and early strength achievement. It meets the ASTM requirements for high range water reducing admixtures (BASF, 2015).

3.2.2. Sample preparation and curing

A number of CPB samples made from different tailings types and varying dosage of the Master G superplasticizer were prepared. Summary of the experimental plan is presented in Table 3.4. The tailings were first mixed with the binder in a mechanical mixer for 2 min. The water containing an appropriate percentage of the admixture was then added and the CPB further mixed for an additional 5 min to obtain a homogeneous paste. To understand the rheology of CPB under different conditions, the initial and curing temperatures of the CPB were controlled at 2 °C, 20 °C and 35 °C. These temperatures have been selected to cover a wide range of temperatures to which the CPB can be subjected during transport due to several factors or mechanisms (cement hydration heat, geographical location of the mine, deep mine temperature, geological conditions, etc., (Wu et al., 2013). Pre-weighted ingredients of the CPB were stored in a temperature-controlled chamber (refrigerator or oven, as the case may be) for 24 h to attain the desired temperature.

For both the yield stress and viscosity tests, a cylindrical container of 10 cm diameter and 20 cm height was used. This satisfies the dimension requirements for the vane shear apparatus used for measuring the yield stress as per ASTM D4648/D4648M-16 and for the Viscometer used for measuring the viscosity (Brookfield, n.d.). Freshly prepared CPB was poured into the cylinders which were then sealed and stored in the temperature-controlled chamber. Before each measurement, the specimen was agitated for about 1 min to simulate the constant agitation of the CPB during transportation.

Table 3.4. Summary of mix composition for specimens used

Test	Tailings type	Binder	Binder content (%)	W/C ratio	Admixture content (%)	Curing Temperature (ºC)
Yield stress, viscosity test, and pH	ST	PCI	4.5	7.35	0, 0.05, 0.125, 0.25	2, 20, 35
	ST, LSG, TP	PCI	4.5	7.35	0	20
Monitoring for electrical conductivity, volumetric water content, temperature, and suction	ST	PCI	4.5	7.35	0, 0.25	2, 20, 35
Microstructural analysis	-	PCI	100	1.0	0	2, 20, 35
Zeta potential	ST	PCI	4.5	7.35		20

ST: silica tailings; LSG: Lake Shore Gold tailings; TP: Tailing ponds tailings; PCI: Portland cement type I; WC ratio: the ratio of the mass of water to the mass of the binder

3.3 Testing and monitoring of specimens

3.3.1. Yield stress measurements

Wykeham-Ferrance laboratory vane shear apparatus with a four-bladed vane (2.5 cm in diameter and 2.5 cm in height) and a calibrated torsion spring was used for the yield stress measurement. The vane test using such apparatus was first developed for shear strength measurement for cohesive soils but now widely being used for yield stress measurement for non-Newtonian fluids (Keentok, 1982; Nguyen and Boger, 1985). With a single-point measurement, the yield stress of a viscous fluid can easily be determined (Nguyen and Boger, 1985; Dzuy and

Boger, 1985; Xiopeng et al., 2019). The following steps were followed to determine the yield stress:

- The vane was gently inserted into the middle of the test container.
- The specimen was allowed to stabilize for 30 s due to the disturbance from the vane insertion (Saebimoghaddam, 2005).
- The motor was then turned on, driving the vane slowly at a constant speed of 0.18 rpm.
- The maximum torque at which the material sheared was recorded and the corresponding yield stress was determined based on the procedure outlined in the ASTM D4648/D4648M-16.

Using a unique sample for each measurement, the yield stress of fresh CPB was determined at 0, 1, 2, and 4 curing hours. Each test was repeated at least twice to ensure repeatability of results.

3.3.2. Viscosity measurements

The viscosity was measured using Brookfield DV-E digital viscometer (Brookfied, 2016). It allows an instantaneous viscosity measurement through a spindle that is rotated at constant speed by a calibrated spring. This is achieved by monitoring the viscous drag of the fluid with respect to the spindle by a rotary transducer that provides a torque signal that is translated as a spring deflection (Brookfield, 2014). Spindles are chosen based on the viscosity range of the material being tested. For this study, an RV4 spindle was used and each time a specimen was being tested, an appropriate rotor speed was selected to ensure that the recorded viscosity is within an acceptable limit. The spindle was first inserted into the spacemen gently in a tilted position (to avoid air trapping) and centered. A guard leg was mounted before attaching the spindle to the spindle coupling nut of the device. The viscometer was then turned on and the reading was allowed to stabilize before recording. Similarly, samples were tested at 0, 1, 2 and 4 curing hours, at least twice each time to ensure repeatability of results.

3.3.3. Microstructural analyses

To have a better understanding of the influence of the superplasticizer and curing temperature on the cement hydration process, thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were conducted on cement paste specimens cured in the same condition as the CPB. The test was performed using thermogravimetric analyzer incorporated with a differential scanning calorimeter (SDT) that monitors and records weight change, heat flow, and temperature transition in the sample. The specimens were cured for 4 h and oven-dried at 45 °C until a constant mass was attained.

3.3.4. Zeta potential test and pH measurements

Zeta potentials of CPB samples treated with a different dosage of the superplasticizer were measured using Malvern Zetasizer Nano series. The device measures the electrophoretic mobility of suspended particles based on phase analysis light scattering (PALS). The zeta potential of the particles is evaluated using the Henry equation (Clogston and Patri, 2011). Each zeta potential measurement was repeated at least three times to ensure result repeatability. Likewise, the pH was measured using Oakton pHTestr 10 with an accuracy of 0.01 (Oakton, 2018). The pH measurement procedure by using using Oakton pHTestr 10 is described in (Plank et al., 2005). Similarly, at least two measurements were taken to ensure results repeatability.

3.3.5. Monitoring program

To gain additional insight into the reaction mechanisms responsible for the rheological behavior of the CPB with varying composition, a 5TE sensor was used to monitor the electrical conductivity (EC), volumetric water content (VWC), and temperature while an MPS-6 sensor was used for suction. The evolution of EC in the specimens is a good measure of ion movement due to the chemical reactions and water content in the CPB. For the EC measurement, the sensor has an accuracy of ±10% with a value range from 0 dS/m to 23 dS/m. The VWC measurement ranges between 0 m^3/m^3 and 100 m^3/m^3 with an accuracy of ±3%. It is important for tracking water consumption by cement hydration process in the CPB. Likewise, the sensor records temperature within the range of -40 °C to 60 °C with an accuracy of ±1 °C. On the hand, the MPS-6 sensor allows suction measurement in the range of −9 kPa to −100 kPa with an accuracy of ±10%. Each sensor was placed at the middle of a plastic cylindrical container of 10 cm diameter by 20 cm height filled with the CPB and readings recorded from the time of cast until 4 h. An EM50 data logger was used for recording the data.

3.3. Results and discussions

3.3.1. Time-dependent evolution of the rheological properties of CPB with superplasticizer

Yield stress and viscosity were used to study the rheology of fresh CPB made with different proportions of the Master Glenium superplasticizer. As shown in Fig. 1., the viscosity of the CPB without the admixture is much higher than that with 0.05, 0.125, and 0.25% at the early stage of preparation. With a moderate addition of 0.125%, the viscosity was lowered from 2.3 Pa.s to about 1.1 Pa.s at 0 h and this trend continues over the rest of the curing period. Likewise, the evolution of yield stress within the first 4 h of mixing is presented in Fig. 2. In the same way, the introduction of the admixture results in a proportional decrease in yield stress of the CPB. The reduction is even more pronounced at the 4 h curing time, with the yield stress being reduced from 750 Pa to 275 Pa with 0.125% admixture content and to 143 Pa with 0.25% admixture content. This increase in fluidity observed from the two rheological properties can be associated with the dispersion of effect of high range WRAs. Superplasticizers made from carboxylic compounds, such as the

Master Glenium, introduce two types of repulsive forces between the cement particles: a) electrostatic repulsion due to negative charges from the carboxylic group, and b) a steric repulsion associated with the long polymer chains in the compound 05 (Pereira et al., 2012; Plank et al., 2005). This is supported by the zeta potentials of the CPB with and without the admixture as can be seen in Fig. 3. The CPB containing 0.05% admixture has a zeta potential of about −10 mV as opposed to the −3.5 mV for the untreated sample. This suggests that the inter-particle repulsive force is much higher in the presence of the superplasticizer (Uchikawa et al., 1997; Hyunh et al., 2006; Ferrari et al., 2014).

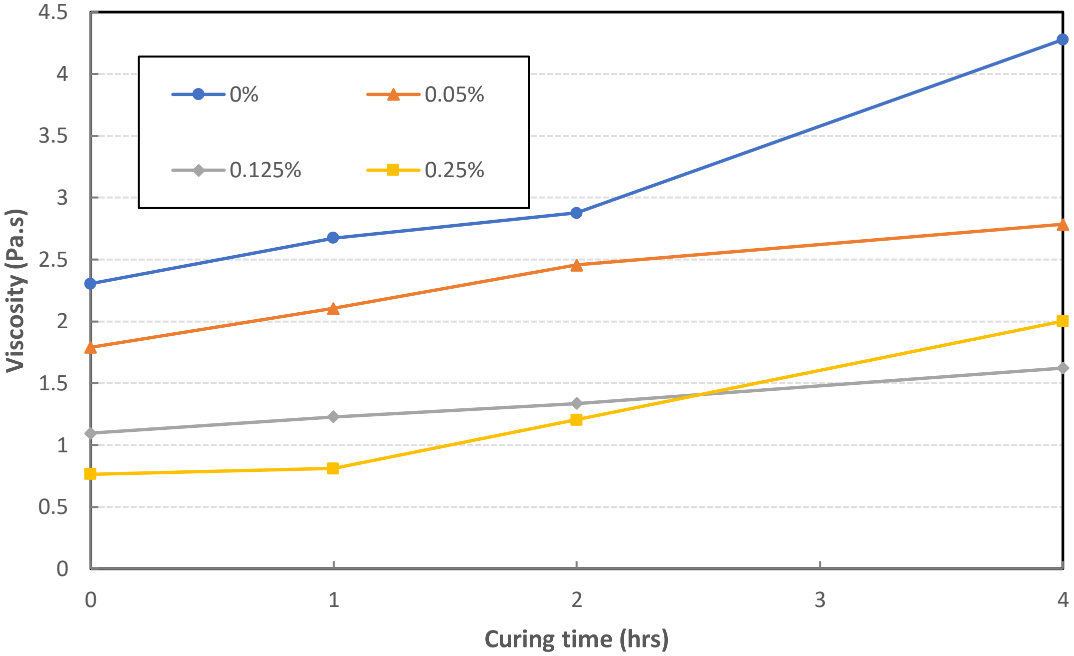


Figure 3.1. Time-dependent evolution of viscosity of CPB containing different dosages of superplasticizer at room temperature

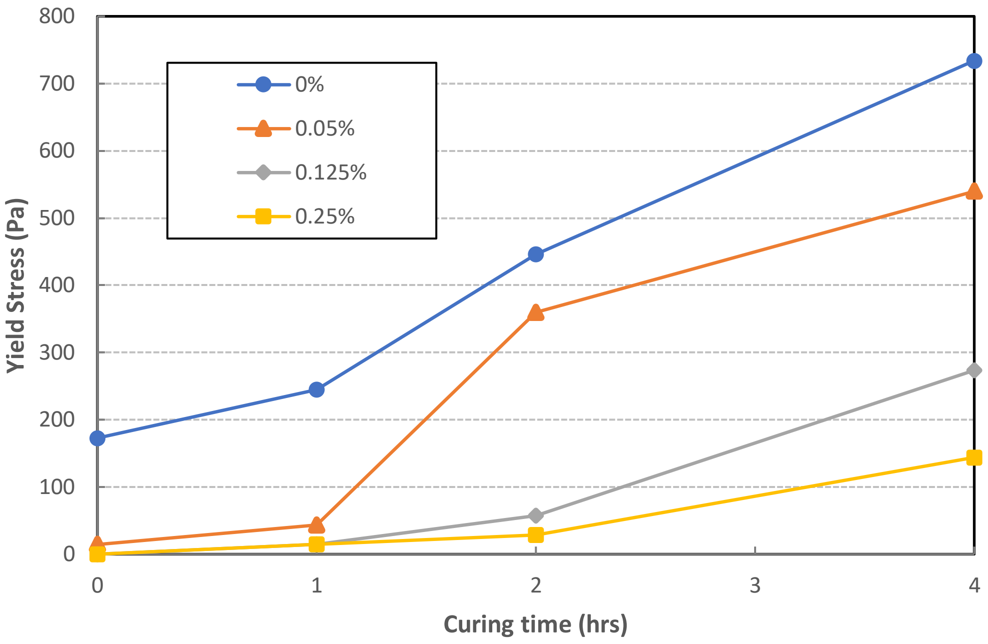
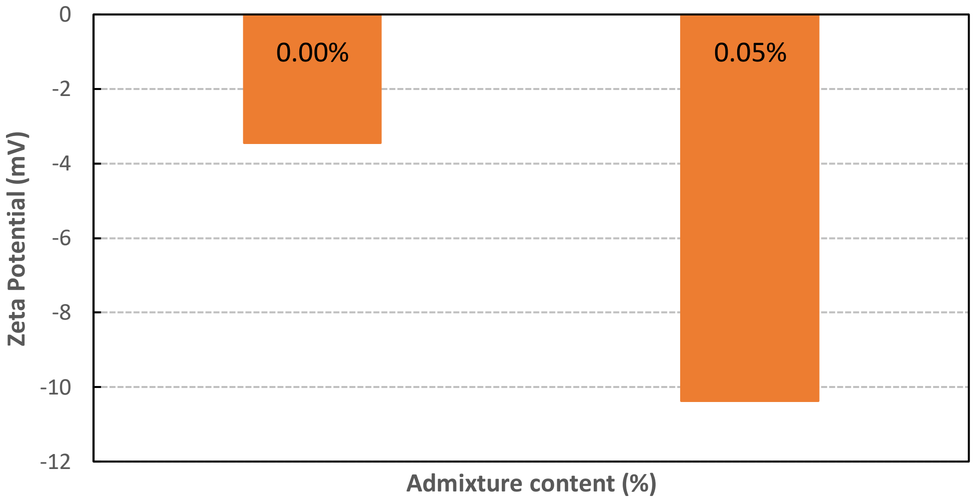
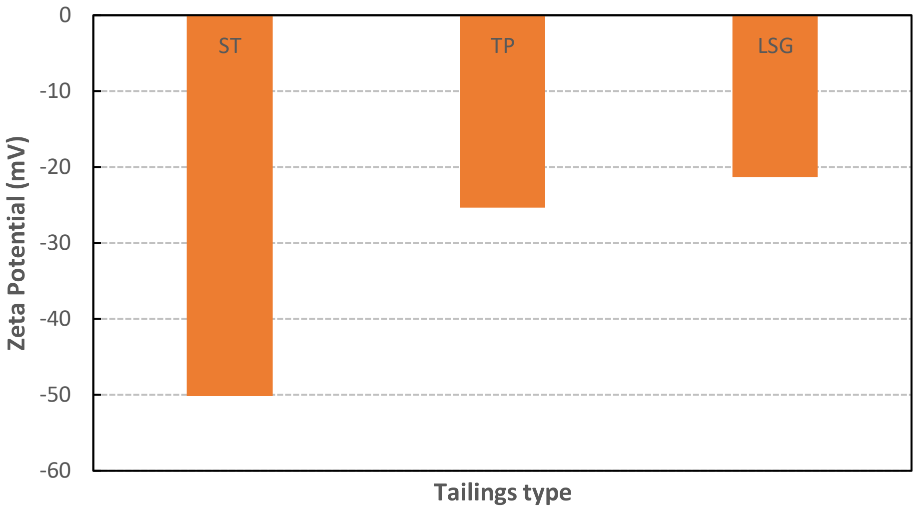


Figure 3.2. Time-dependent evolution of yield stress of CPB containing different dosages of superplasticizer at room temperature



a) CPB made with different admixture content



b) CPB made with different tailings type

Figure 3.3. Effect of the superplasticizer and tailings type on the zeta potential of fresh CPB

An additional explanation for the change of flowability of the CPB due to the addition of superplasticizers is their influence on cement hydration. As the repulsive force between the cement particles increases, less hydration by-products are generated, and with less solid content the CPB becomes less viscous (Wu et al., 2015; Wu et al., 2013). The TG/DTG diagrams of cement paste samples containing different admixture proportions and cured for 4-hours shown in Fig. 4 supports this assertion. The graphs confirm that more hydration products are produced within the CPB without admixture. Indeed, the first two peaks (sudden change in weight) which occurred at about 100 °C and 400 °C indicate highest weight loss is from the sample containing 0% superplasticizer followed by that containing 0.125% and lastly the mix containing 0.25%. The first peak is associated with the formation of products such as calcium-silicate-hydrate (C-S-H), ettringite, and gypsum while the second peak is due to the dihydroxylation of calcium hydroxide (CH) respectively (Zhou and Glasser, 2001; Gomes et al., 2005; Fall et al., 2010; He et al., 2014). The third peak that occurred at about 750 °C is related to the decomposition of the calcite in the cement (Zhou and Glasser, 2001; Fall et al., 2010). The lower peaks associated with the treated CPB samples mean that much fewer solid products are formed during the hydration process in the presence of the superplasticizer. Moreover, the EC monitoring results in Fig. 5 supports the assertion that the superplasticizer slows down the hydration reaction. The EC of the CPB containing 0.25% superplasticizer is significantly lower than the CPB containing 0%. Thus, there is higher mobility of ions in the CPB without the admixture. It can also be seen from Fig. 6 that the specimens without the superplasticizer maintained higher temperature over the curing period, further reinforcing indicating slower hydration rate that is accompanied by heat generation (Shi and Zheng, 2007; Nasir and Fall, 2009; Wu et al., 2013).

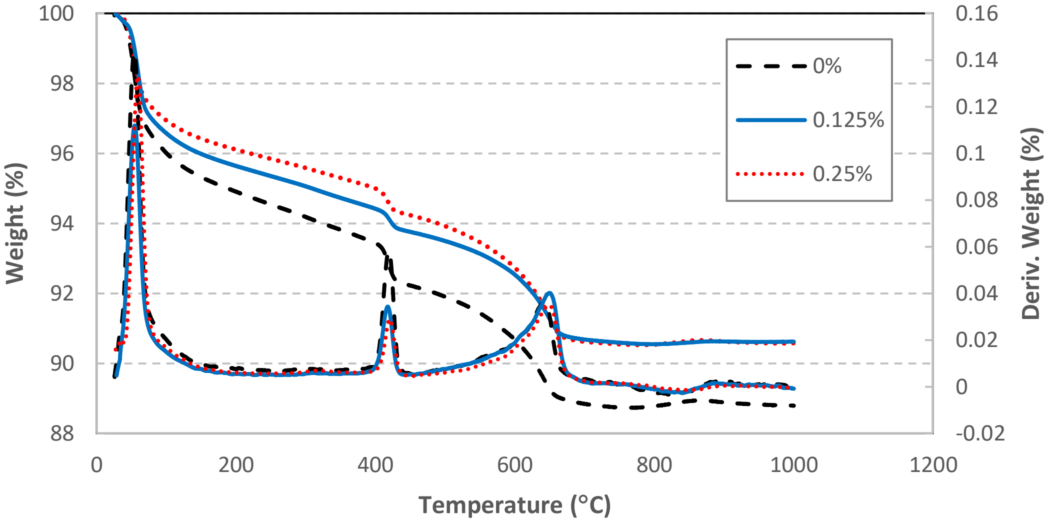


Figure 3.4. TG/DTG diagrams for 4-hour cement paste containing different admixture contents

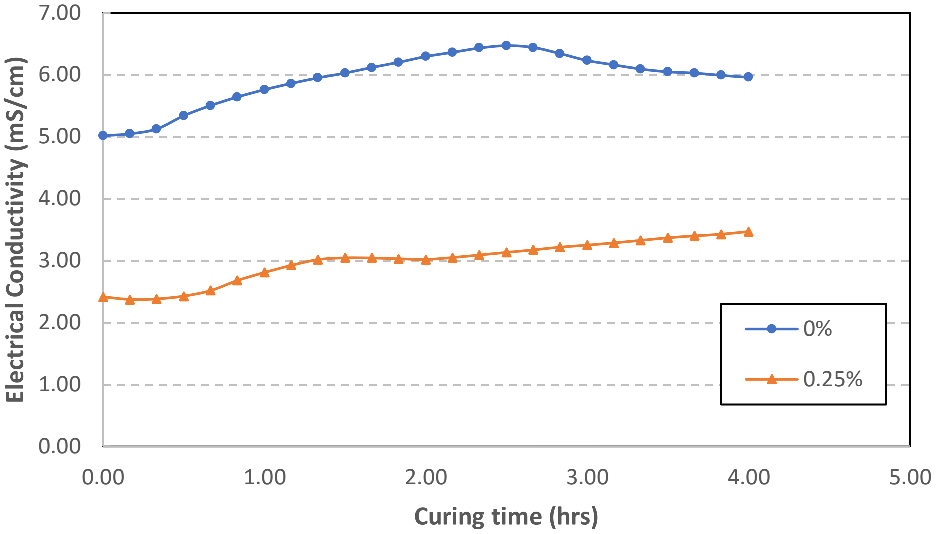


Figure 3.5. Development of electrical conductivity in CPB containing different dosages of superplasticizer

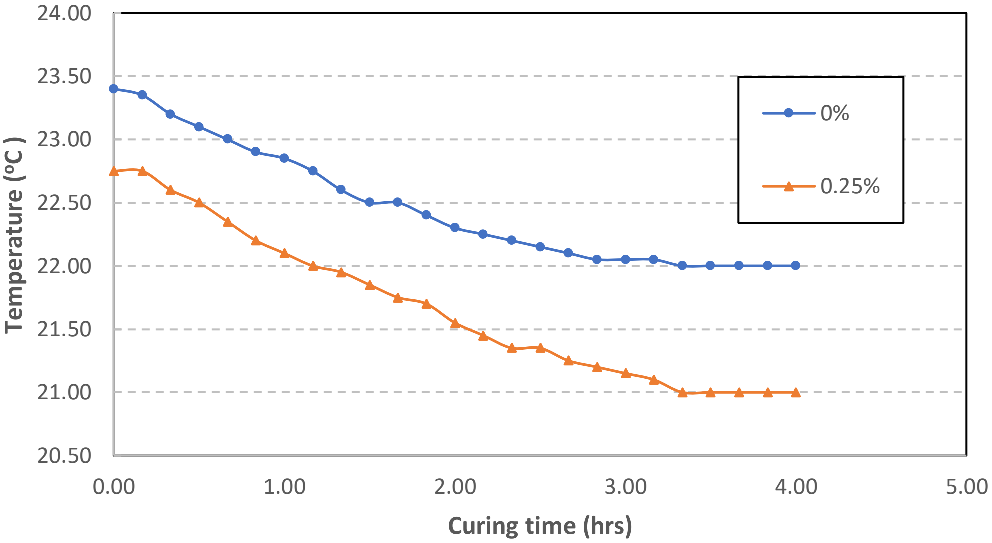


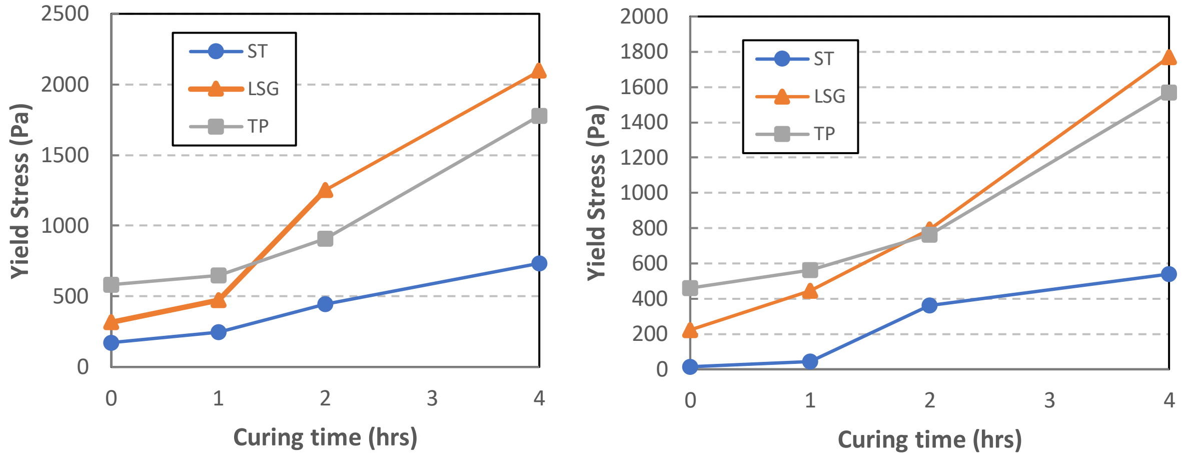
Figure 3.6. Evolution of temperature in CPB containing different dosages of superplasticizer

It can also be observed from Fig. 1, Fig. 2 that both yield stress and viscosity of the CPB samples increase steadily with the passage of curing time. This time-dependent increase in yield stress is also largely attributed to the cement hydration process. The chemical reaction generally begins as soon as the cement comes in contact with water (Aïtcin, 2000; Cui and Fall, 2016; Marchon and Flatt, 2016). Coupled with the surface absorption by the poorly crystalline C-S-H gel, this translates to the consumption of the free water in the CPB mix and subsequently leading to its thickening (Bensted, 1983; Tariq and Nehdi, 2007; Cui and Fall, 2015; Marchon and Flatt, 2016). Furthermore, the cement hydration produces primary ettringite that fills the pores between the solid particles in the CPB and thereby restricting their movement (Ghirian and Fall, 2014; Xiaopend et al., 2019).

3.3.2. Effect of tailings type on the yield stress of CPB with superplasticizer

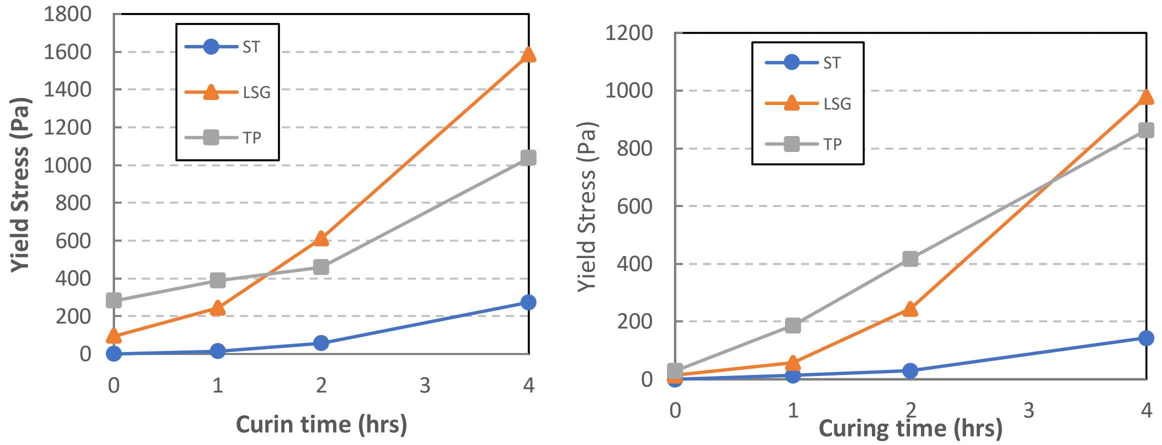
The performance of the Master Glenium superplasticizer was also investigated on CPB samples made with different tailings and the results are presented in Fig. 7. The artificial tailings (ST) exhibited the lowest yield stress in the control samples as well as in the all the CPB samples containing the admixture. For the control samples, the CPB with ST reached the highest magnitude of 734 Pa as compared to 1777 Pa and 2094 Pa for TP and LSG respectively. Likewise, its 4-hour yield stress when treated with 0.25% admixture is 143 Pa, much lower than 863 Pa for TP and 978 Pa for LSG. This significant variation is mainly as a result of the differences in the physical properties (Table 1), mineralogical compositions (Table 2) as well as the pore water chemistry of the tailings (Table 3). The natural tailings are slightly denser (higher G_s value) and better graded with particles larger than 0.25 mm. Increase in the proportion of coarser aggregates has been found to increase the yield stress of fresh concrete (Hu and Wang, 2011) as well as thickened tailings (Mizani and Simms, 2016). The pore water chemistry and mineralogical composition are established factors that can influence the rheology of a solution by changing the magnitude of inter-particle forces (Leong and Boger, 1990; Yin et al., 2012; Simon and Grabinsky, 2013).

Generally, if the net inter-particle force is an attraction, the solid particles (i.e. aggregates) would flocculate thereby increasing the yield stress (Leong and Boger, 1990). Based on the zeta potential values of CPB made with the three tailings (Fig. 3b), it can be seen that the ST-CPB has the highest zeta potential of −50 mV as compared to the −25 mV for TP and −21 for LSG. Larger negative zeta potential indicates a higher electric double layer repulsive force (Simon and Grabinsky, 2013).



a) 0% admixture content

b) 0.05% admixture content



c) 0.125% admixture content

d) 0.25% admixture content

Figure 3.1. Effect of tailings type on the yield stress of CPB containing 0.125% of superplasticizer

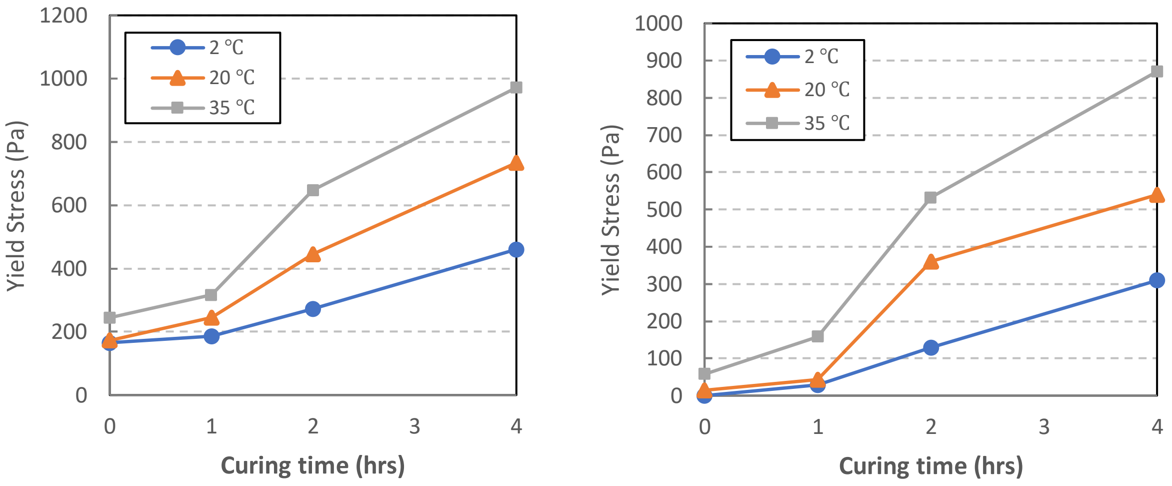
Between the two natural tailings, CPB made from the TP tailings has higher yield stress than that made from LSG tailings within the first hour of mixing but become lower thereafter. This is true for all the dosages of the superplasticizer except at 0.25% where it only becomes lower after 4 h of curing. The higher proportion of sulphate ions (So_4^{2-}) in the pore water of the TP tailings (Table 3) may be partly responsible for that. Some studies have shown that sulphates can react with calcium hydroxide and tricalcium aluminate to produce secondary gypsum and ettringite, respectively (Hassani et al., 2001; Kesimal et al., 2004; Tariq and Nehdi, 2007; Ercikdi et al., 2010; Pokharel and Fall, 2010). On the other hand, the yield stress of the LSG-CPB becoming higher at 4 h could be due to the influence of other properties such as the tailings gradation and density (Hu and Wang, 2011) becoming the principal determinants of the flowability after few hours, when the chemical interaction slows down (Pokharel and Fall, 2010; Deng et al., 2018).

3.3.3. Effect of temperature on the time-dependent evolution of the rheological properties of CPB with superplasticizers

The development of the viscosity and yield stress of fresh CPB containing different dosages of superplasticizer and cured under the temperatures of 2 °C, 20 °C (room temperature) and 35 °C is illustrated in Fig. 6. The time-dependent increase in both rheological properties is consistent with what has been observed earlier. In addition, it is evident from the results that the curing temperature has a direct relationship with the viscosity and yield stress. The temperature-induced increase is consistent regardless of the percentage of superplasticizer used, although it is more pronounced with the passage of time. That is to say that at the time of mixing, the yield stress and viscosity values under the three curing temperatures are closer than after 4 h of curing. With the addition of 0% superplasticizer, initial yield stress at 2 °C, 20 °C, and 35 °C was respectively

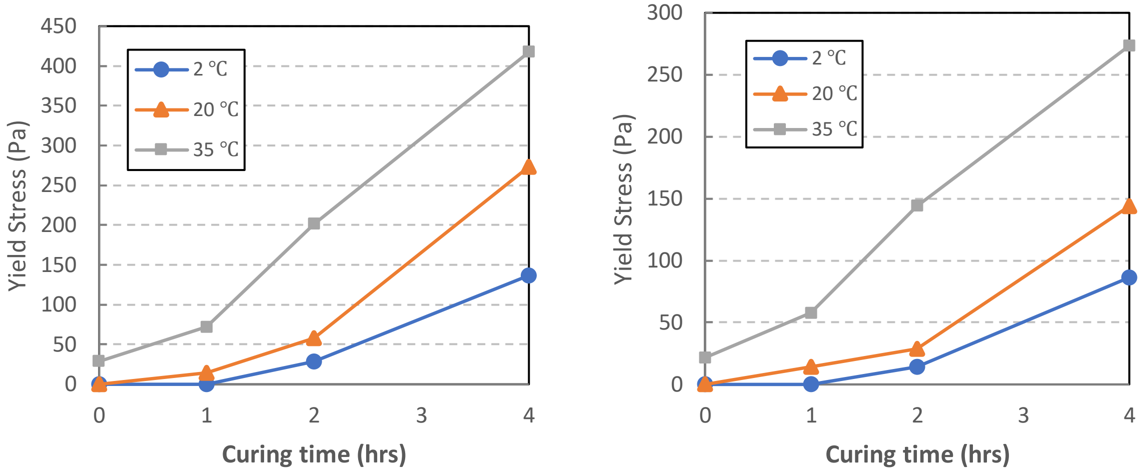
165 Pa, 172 Pa, and 244 Pa. After 4 h of curing, the yield stress recorded was 532 Pa, 734 Pa, and 812 Pa. Similarly, with the addition of 0.25% superplasticizer, the yield stress was 0 Pa, 0 Pa, and 22 Pa at 0 h which increased to 29 Pa, 143 Pa, and 273 Pa after 4 h. A similar trend is also true for the viscosity of CPB as shown in Fig. 9. This rapid increase is largely due to the acceleration of cement hydration under higher temperature (Pokharel and Fall, 2010; Marchon and Flatt, 2016) as supported by the EC monitoring results. From Fig. 12, it can be observed that the CPB cured at 2 °C maintained the lowest EC over the 4-hour period, followed by the 20 °C curing. This is an indication that concentration and mobility of ions increase at high temperature. Because the hydration reaction uses off the available free water (Wang et al., 2016), the CPB becomes more viscous. Evidence of this can be seen from the increase of suction in the CPB samples at a higher temperature as shown in Fig. 13. Furthermore, cement hydration products (e.g., C-S-H, ettringite, and CH) are generated faster at higher curing temperature resulting in faster thickening of the CPB (Fall et al., 2010; Haiqiang et al., 2016; Marchon and Flatt, 2016). This is supported by the TG/DTG diagram for two cement paste samples cured at different temperatures (Fig. 10). As it can be observed, the weight loss for both first and second peaks is significantly higher for the cement paste cured at 35 °C than that cured at 20 °C.

The yield stress and viscosity results (Fig. 8, Fig. 9) also show that different proportions of superplasticizer are required to achieve certain flowability at different temperatures. For example, the 4-hour yield stress of CPB containing 0% superplasticizer and cured at 2 °C (450 Pa) is comparable to that of the 4-hour yield stress of the CPB containing 0.125% and cured at 35 °C (420 Pa). The same observation is true for the viscosity, indicating that temperature has a significant influence on the performance of the superplasticizer. Under elevated temperature, there are two opposing factors that have been found to affect the fluidity of a cementitious material containing superplasticizer: a) an increase in the superplasticizer adsorption which increases the flowability (Nawa et al., 2000; Łukowski, 2016); b) an increase in the amount hydration products which decreases the flowability (Nawa et al., 2000; Ghafoori and Diawara, 2010). The evidence of increased admixture adsorption can be seen from the pH result in Fig. 11b. The CPB containing 0.125% superplasticizer becomes less alkaline at high temperature with a smaller margin than the CPB containing 0% superplasticizer (a drop of 0.26 as opposed to 0.30 at 0 h and 0.31 as opposed to 0.34 at 4 h). Thus, in addition to the drop solely due to temperature rise, there is more unadsorbed superplasticizer in the free water resulting in a further drop in pH. It is important to note that the superplasticizer has a pH ranging from 6 to 7. Nevertheless, the decrease in flowability due to the second factor (the mechanism was discussed earlier) governs the rheological behavior of the CPB (Griesser, 2002; Heikal et al., 2005; Łukowski, 2016; Wang et al., 2018).



a) 0% admixture content

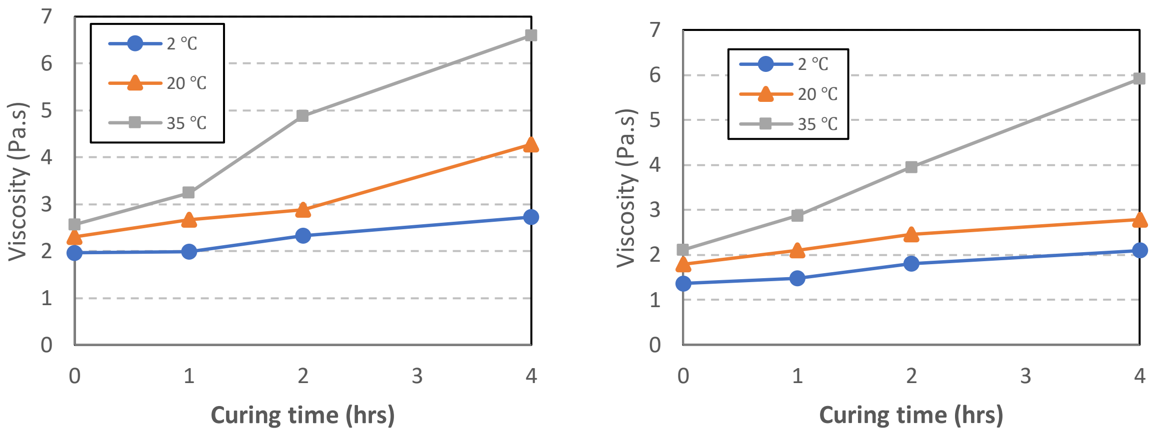
b) 0.05% admixture content



a) 0.125% admixture content

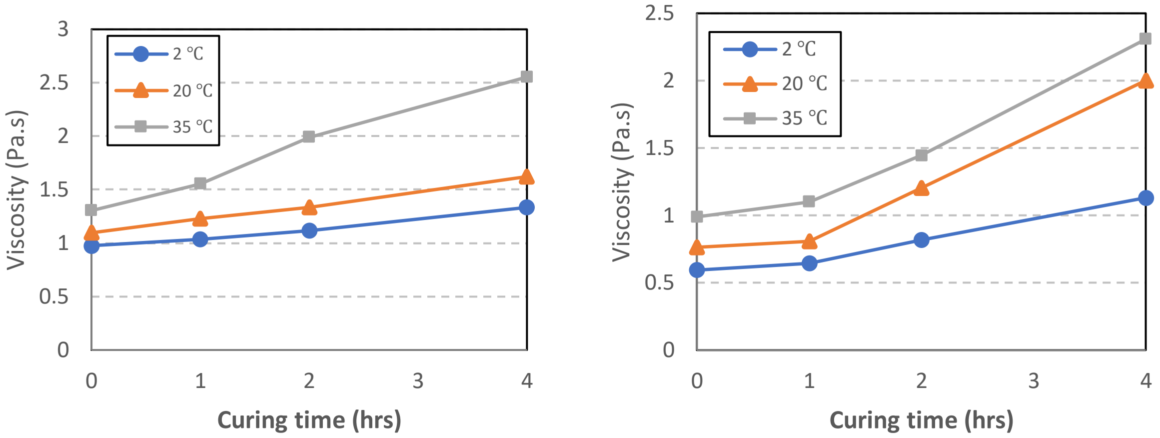
d) 0.25% admixture content

Figure 3.8. Time-dependent evolution of the yield stress of CPB at different curing temperatures



b) 0% admixture content

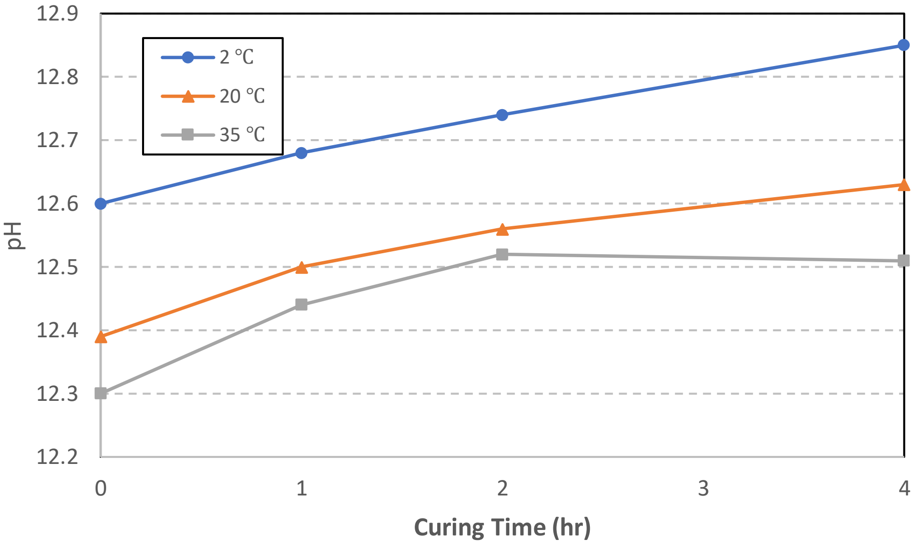
b) 0.05% admixture content



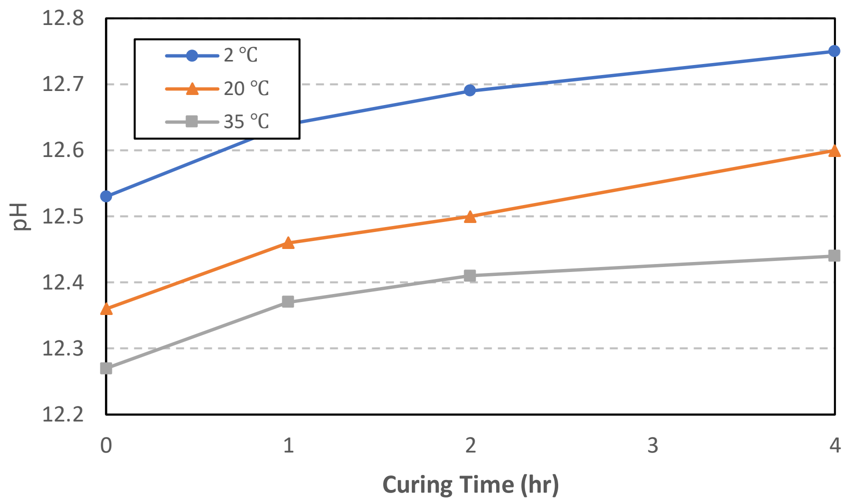
b) 0.125% admixture content

d) 0.25% admixture content

Figure 3.9. Time-dependent evolution of the viscosity of CPB at different curing temperatures



a) 0% admixture content



b) 0.125% admixture content

Figure 3.10. Time-dependent evolution of the pH of fresh CPB at different curing temperatures

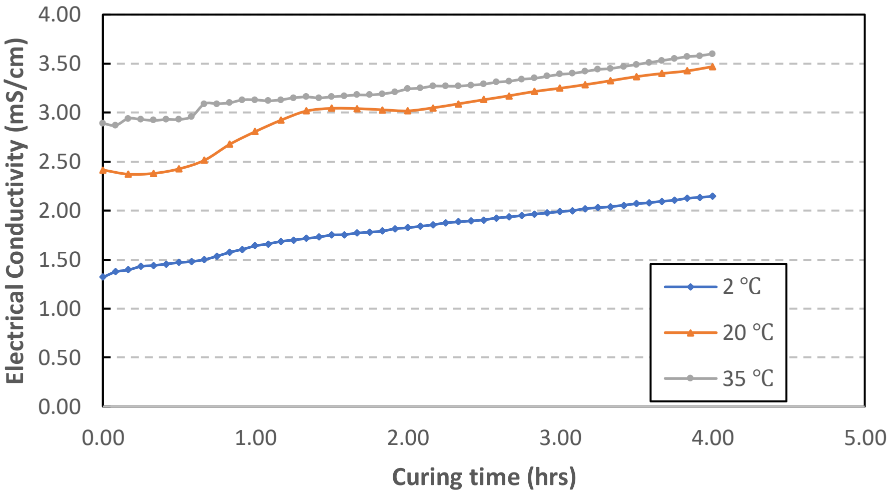


Figure 3.11. Evolution of electrical conductivity of fresh CPB containing 0.125% plasticizer at different curing temperatures

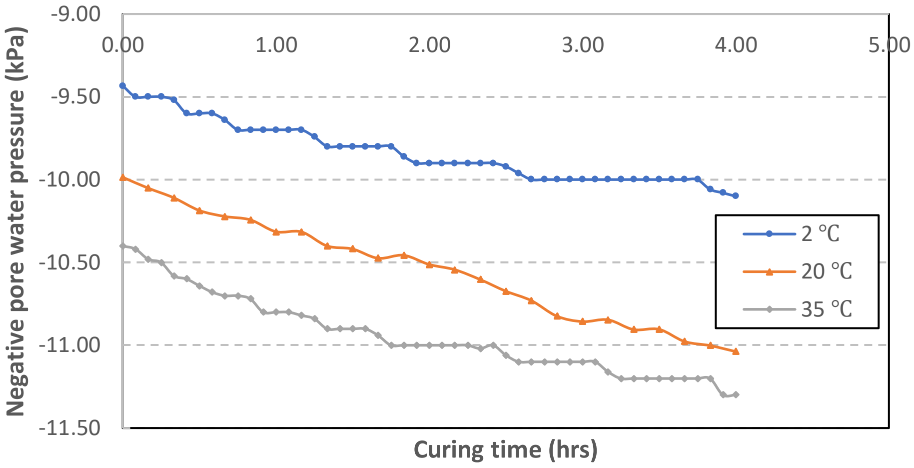


Figure 3.12. Evolution of matric suction of fresh CPB containing 0.125% plasticizer at different curing temperatures

3.4. Summary and conclusions

The time-dependent rheological properties of fresh CPB treated with the Master Glenium superplasticizer and cured under different temperature conditions were studied in this paper. Specimens were prepared with artificial tailings and two types of natural tailings. Superplasticizer dosages of 0, 0.05, 0.125, and 0.25% of the total CPB weight were used. The specimens were cured for 4 h under three different ambient temperatures conditions (2 °C, 20 °C, and 35 °C). Additional tests such as pH, thermal analysis and zeta potential analysis were conducted to understand the reasons behind the nature of the results observed. The major conclusions based on the results obtained are summarized below.

1. Generally, both the viscosity and the yield stress of CPB, whether with superplasticizer or not, increase with the increase of curing time. However, the change is slower in the CPB containing superplasticizer.

2. Addition of superplasticizer to the CPB significantly reduces the yield stress and viscosity of CPB for both artificial and natural tailings. An addition of 0.125% of the

admixture results in over 50% reduction in yield stress at the time of preparation as well as after 4 h. A similar reduction was observed in the improvement of viscosity. The marginal reduction upon increasing the admixture to 0.25% is much less, indicating that 0.125% is the most effective proportion from the percentages used in the study.

3. CPB samples made of natural tailings exhibit higher yield stress and viscosity than artificial tailings due to their mineralogical compositions and pore water chemistry. Thus, different quantities of superplasticizer are required for different tailings type to achieve the same flowability improvement.

4. The curing temperature has a significant influence on the rheology of CPB even when treated with superplasticizer. An increased superplasticizer dosage is required to prepare sufficiently fluid CPB at elevated temperatures.

3.5. References

Aïtcin, P. C. (2000). Cements of yesterday and today: concrete of tomorrow. *Cement and Concrete research*, *30*(9), 1349-1359.

BASF. (2015). MasterGlenium 7500 Full-range water-reducing admixture. Web. https://www.master-builders-solutions.basf.us/en-us/products/concrete-admixtures/water-reducers/water-reducers-high-range/masterglenium-7500

Bensted, J. (1983). Hydration of Portland cement. In *Advances in cement technology* (pp. 307 347).

Barabanshchikov, Y. G., & Komarinskiy, M. V. (2014). Influence of superplasticizer S-3 on the technological properties of concrete mixtures. Advanced Materials Research, 941.

Bravo, M., de Brito, J., Evangelista, L., & Pacheco, J. (2017). Superplasticizer's efficiency on the mechanical properties of recycled aggregates concrete: Influence of recycled aggregates composition and incorporation ratio. *Construction and Building Materials*, *153*, 129-138.

Brookfield (n.d.) DV-E Digital viscometer: Operating instructions. Middleboro, USA. Web. https://pim-resources.coleparmer.com/instruction-manual/98945-xx.pdf

Clogston, J. D., and Patri, A. K. 2011. Zeta potential measurement. *Characterization of nanoparticles intended for drug delivery*, 63-70.

Deng, X. J., Klein, B., Zhang, J. X., Hallbom, D., & de Wit, B. (2018). Time-dependent rheological behaviour of cemented backfill mixture. International Journal of Mining, Reclamation and Environment, 32(3), 145-162.

Dzuy, N. Q., & Boger, D. V. (1985). Direct yield stress measurement with the vane method. *Journal of rheology*, *29*(3), 335-347.

Ercikdi, B., Cihangir, F., Kesimal, A., Deveci, H., & Alp, İ. (2010). Utilization of water-reducing admixtures in cemented paste backfill of sulphide-rich mill tailings. *Journal of hazardous materials*, *179*(1-3), 940-946.

Ercikdi, B., Külekci, G., & Yılmaz, T. (2015). Utilization of granulated marble wastes and waste bricks as mineral admixture in cemented paste backfill of sulphide-rich tailings. *Construction and Building Materials*, *93*, 573-583.

Elaty, M. A. A., and Ghazy, M. F. (2012). Flow properties of fresh concrete by using modified geotechnical Vane shear test. *HBRC Journal*, *8*(3): 159-169.

Fall, M., Benzaazoua, M. and Saa, E.G., 2008. Mix proportioning of underground cemented tailings backfill. *Tunnelling and Underground space technology*, *23*(1), pp.80-90.

Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. Engineering Geology, 114(3), 397-413.

Ferrari, L., Kaufmann, J., Winnefeld, F., & Plank, J. (2014). Impact of particle size on interaction forces between ettringite and dispersing comb-polymers in various electrolyte solutions. *Journal of colloid and interface science*, *419*, 17-24.

Ghafoori, N., & Diawara, H. (2010). Influence of temperature on fresh performance of self consolidating concrete. *Construction and Building Materials*, *24*(6), 946-955.

Ghirian, A., & Fall, M. (2014). Coupled thermo-hydro-mechanical–chemical behaviour of cemented paste backfill in column experiments: Part II: Mechanical, chemical and microstructural processes and characteristics. *Engineering Geology*, *170*, 11-23.

Gomes, C. E. M., Ferreira, O. P., & Fernandes, M. R. (2005). Influence of vinyl acetate-versatic vinylester copolymer on the microstructural characteristics of cement pastes. *Materials Research*, *8*(1), 51-56.

Griesser, A. (2002). *Cement-superplasticizer interactions at ambient temperatures: rheology, phase composition, pore water and heat of hydration of cementitious systems* (Doctoral dissertation, ETH Zurich).

Haiqiang, J., Fall, M., & Cui, L. (2016). Yield stress of cemented paste backfill in sub-zero environments: experimental results. *Minerals Engineering*, *92*, 141-150.

Hassani, F. P., Ouellet, J., & Hossein, M. (2001). Strength development in underground high sulphate paste backfill operation. *CIM bulletin*, 57-62.

He, X. F., Miao, C. W., Wu, Y. H., Cao, X. X., & Liu, D. (2014). Thermal Reaction Kinetics of Fly Ash Cement Paste at the Age of 28 Days. In *Applied Mechanics and Materials* (Vol. 668, pp. 91-94). Trans Tech Publications.

Heikal, M., Morsy, M. S., & Aiad, I. (2005). Effect of treatment temperature on the early hydration characteristics of superplasticized silica fume blended cement pastes. *Cement and Concrete Research*, *35*(4), 680-687.

Hu, J., & Wang, K. (2011). Effect of coarse aggregate characteristics on concrete rheology. Construction and Building Materials, 25(3), 1196-1204.

Huynh, L., Beattie, D. A., Fornasiero, D., & Ralston, J. (2006). Effect of polyphosphate and naphthalene sulfonate formaldehyde condensate on the rheological properties of dewatered tailings and cemented paste backfill. *Minerals engineering*, *19*(1), 28-36.

Jiang, H., Fall, M., & Cui, L. (2017). Freezing behaviour of cemented paste backfill material in column experiments. *Construction and Building Materials*, *147*, 837-846.

Jolicoeur, C., & Simard, M. A. (1998). Chemical admixture-cement interactions: phenomenology and physico-chemical concepts. *Cement and Concrete composites*, *20*(2-3), 87-101.

Jung, S. J., & Biswas, K. (2002). Review of current high density paste fill and its technology. Mineral Resources Engineering, 11(02), 165-182.

Keentok, M. (1982). The measurement of the yield stress of liquids. *Rheologica Acta*, *21*(3), 325-332.

Kesimal, A., Yilmaz, E., & Ercikdi, B. (2004). Evaluation of paste backfill test results obtained from different size slumps with varying cement contents for sulphur rich mill tailings. *Cement and Concrete Research*, *34*(10), 1817-1822.

Kong, D. L., & Sanjayan, J. G. (2010). Effect of elevated temperatures on geopolymer paste, mortar and concrete. Cement and concrete research, 40(2), 334-339.

Leong, Y. K., & Boger, D. V. (1990). Surface chemistry effects on concentrated suspension rheology. *Journal of colloid and interface science, 136*(1), 249-258.

Liu, Q., Liu, D., Liu, X., Gao, F. and Li, S., 2016. Research and application of surface paste disposal for clay-sized tailings in tropical rainy climate. *International Journal of Mineral Processing, 157*, pp.227-235.

Łukowski, P. (2016). Influence of temperature on efficiency of superplasticizing admixtures for concrete. *Journal of Building Chemistry*, *1*(1), 32-36.

Marchon, D., & Flatt, R. J. (2016). Mechanisms of cement hydration. In Science and technology of concrete admixtures (pp. 129-145).

Mizani, S., & Simms, P. (2016). Method-dependent variation of yield stress in a thickened gold tailings explained using a structure based viscosity model. *Minerals engineering, 98*, 40-48.

Nasir, O., & Fall, M. (2009). Modeling the heat development in hydrating CPB structures. *Computers and Geotechnics*, *36*(7), 1207-1218.

Nawa, T., Ichiboji, H., & Kinoshita, M. (2000). Influence of temperature on fluidity of cement paste containing superplasticizer with polyethylene oxide graft chains. Special Publication, 195, 181-194.

Ouellet, S., Bussière, B., Aubertin, M., & Benzaazoua, M. (2007). Microstructural evolution of cemented paste backfill: Mercury intrusion porosimetry test results. *Cement and Concrete Research*, *37*(12), 1654-1665.

Pereira, P., Evangelista, L., & De Brito, J. (2012). The effect of superplasticisers on the workability and compressive strength of concrete made with fine recycled concrete aggregates. Construction and Building Materials, 28(1), 722-729.

Plank, J., Vlad, D., Brandl, A., & Chatziagorastou, P. (2005). Colloidal chemistry examination of the steric effect of polycarboxylate superplasticizers. Cement International, 3(2), 100-110.

Pokharel, M., & Fall, M. (2010). Coupled thermochemical effects on the strength development of slag-paste backfill materials. *Journal of Materials in Civil Engineering*, *23*(5), 511-525.

Şahmaran, M., Christianto, H. A., & Yaman, İ. Ö. (2006). The effect of chemical admixtures and mineral additives on the properties of self-compacting mortars. *Cement and concrete composites*, *28*(5), 432-440.

Saebimoghaddam, A. (2005). *Rheological Yield Stress Measurements of Mine Paste Fill Material* (Doctoral dissertation, McGill University).

Shi, C., He, T. S., Zhang, G., Wang, X., & Hu, Y. (2016). Effects of superplasticizers on carbonation resistance of concrete. *Construction and Building Materials*, *108*, 48-55.

Shi, C., & Zheng, K. (2007). A review on the use of waste glasses in the production of cement and concrete. *Resources, Conservation and Recycling*, *52*(2), 234-247.

Simon, D., & Grabinsky, M. (2013). Apparent yield stress measurement in cemented paste backfill. *International Journal of Mining, Reclamation and Environment*, *27*(4), 231-256.

Tariq, A., & Nehdi, M. (2007, November). Developing durable paste backfill from sulphidic tailings. In *Proceedings of the Institution of Civil Engineers-Waste and Resource Management* (Vol. 160, No. 4, pp. 155-166). Thomas Telford Ltd.

Uchikawa, H., Hanehara, S., & Sawaki, D. (1997). The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture. *Cement and Concrete Research*, *27*(1), 37-50.

Wang, Y., Fall, M., & Wu, A. (2016). Initial temperature-dependence of strength development and self-desiccation in cemented paste backfill that contains sodium silicate. *Cement and Concrete Composites*, *67*, 101-110.

Wu, D., Fall, M., & Cai, S. J. (2013). Coupling temperature, cement hydration and rheological behaviour of fresh cemented paste backfill. Minerals Engineering, 42, 76-87.

Wu, A., Wang, Y., Wang, H., Yin, S. and Miao, X., 2015. Coupled effects of cement type and water quality on the properties of cemented paste backfill. *International Journal of Mineral Processing*, *143*, pp.65-71.

Yilmaz, E. (2017). Stope depth effect on field behaviour and performance of cemented paste backfills. *International Journal of Mining, Reclamation and Environment*, 1-24.

Yin, S., Wu, A., Hu, K., Wang, Y., & Zhang, Y. (2012). The effect of solid components on the rheological and mechanical properties of cemented paste backfill. Minerals Engineering, 35, 61-66.

Yoshioka, K., Sakai, E., Daimon, M., & Kitahara, A. (1997). Role of steric hindrance in the performance of superplasticizers for concrete. Journal of the American Ceramic Society, 80(10), 2667-2671.

Zhou, Q., & Glasser, F. P. (2001). Thermal stability and decomposition mechanisms of ettringite at< 120 C. *Cement and Concrete Research, 31*(9), 1333-1339.

Chapter 4. Technical paper II - Strength Development of Cemented Tailings Materials Containing Polycarboxylate ether-based Superplasticizer: Experimental Results on the Effect of Time and Temperature

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Abstract

Superplasticizers are widely used in the backfill industry for the improvement of the workability of cemented paste backfill (CPB) while keeping water content low. However, the coupled effects of temperature and curing time on the mechanical strength of CPB with superplasticizers are poorly understood. This paper presents new findings of research conducted to experimentally assess the effects of a polycarboxylate-based superplasticizer on the strength of CPB subjected to varying curing time (1, 3, 7, and 28 days) and temperature (2°C, 20°C, and 35°C). The binders used were Portland cement type I, fly ash and blast furnace slag. Superplasticizer contents of 0, 0.125, and 0.25 percent of the total weight of the CPB were added. Various microstructural analyses and monitoring programs were also conducted to understand the principles behind the patterns in the strength of different CPB samples. The results obtained show that the unconfined compressive strength (UCS) of the CPB containing polycarboxylate-based superplasticizer increases with time. Moreover, the increase in superplasticizer content was observed to improve the UCS of the CPB (0.25% > 0.125% > 0%). The temperature was also observed to play an important role in strength development as the UCS increases with the rise in the curing temperature for all samples. It is also found that the temperature-induced strength increase is more significant for the CPBs that contain the superplasticizer than for those without superplasticizer. It was also observed that the CPB containing superplasticizer maintained a relatively similar strength upon replacing the cement with 50% slag while showing a sharp decline with fly ash. The findings from this study will be useful towards a cost-effective design of backfill structures.

Keywords: superplasticizer; tailings**;** cemented paste backfill; mine; temperature; strength; cementitious materials

4.1. Introduction

Sustainable management of a large quantity of tailings produced during the mineral extraction process is a key objective of the cemented paste backfill (CPB) technology. CPB is mainly made up of tailings (70-85% solids), a hydraulic binder, and water (Cui & Fall, 2016; Wu et al., 2015). It offers an innovative way of reusing the tailings to fill the voids left from underground mining and has been associated with a number of economic and environmental benefits. These include the improvement of the speed of mineral ore recovery, provision of a reliably safe working environment for the workers, and ultimately the improvement of the overall efficiency of the mining process (Benzaazoua et al., 2004; Ercridi, Kulekci & Yilmaz, 2015; Jiang, Fall & Cui, 2017). Environmentally, putting the tailings back into the excavated mines eliminates or reduces the threats associated with surface impoundments (e.g., acid mine drainage, leaching of heavy metals, and dam failures) (Driussi & Jansz, 2006; Rico et al., 2008; Yilmaz 2011; Aldhafeeri et al. 2016).

The use of chemical admixtures is prevalent in the construction industry for the improvement of the properties of cementitious materials. Among them are the high range water reducing admixtures, also known as superplasticizers, which are used for workability enhancement without increasing the mixing water. Such admixtures play a vital role in the CPB production whose components are processed in a mixing plant on the ground surface and then pumped to the mine stopes using pipes (Fall & Pokharel, 2010). With the addition of superplasticizers, sufficient flowability can be attained with minimal quantity of mixing water to ensure efficiency in the operation. The enhancement of fluidity is based on the behavior of the organic polymer molecules making up the chemical admixtures, which surround the solid particles in the CPB (through adsorption), leading to dispersion through electrostatic and/or steric forces (Gelardi & Flatt, 2016).

The commonly used superplasticizers are based on lignosulfonate, polycarboxylate, or naphthalene organic compounds, which are characterized by the dispersion mechanism stated (Björnström & Chandra, 2003; Pereira et al., 2012; Bravo et al., 2017). In collaboration with the use of a high proportion of fine aggregates, superplasticizers and the lower range water reducers (plasticizers) have been identified to give self-consolidating concretes their improved workability and strength (Naik et al., 2012; Yahia & Aitcin, 2016). There are ongoing research studies in order to understand the effects of these admixtures on the mechanical characteristics and other behaviors of CPB (e.g. Yang et al., 2018). However, our understanding of the evolution of the mechanical strength of CPB containing superplasticizer cured under varying temperature conditions is still limited. Moreover, the fundamental mechanisms that are responsible for the strength change of CPB with superplasticizer are not well known.

With its global acceptance in the backfill industry, understanding the performance of CPB under different temperature conditions is also essential for its design. Moreover, mine stopes can be very deep and thereby exposing the backfill material to a varying earth-crust temperature (e.g. the Mponeng gold mine in South Africa with a depth exceeding 4 km (Richardson & Jordan, 2002)). Previous research studies have shown that the binder hydration in CPB is greatly influenced by the initial and curing temperature (Nasir & Fall, 2010; Walske et al., 2015; Aldhafeeri et al. 2016; Fang & Fall 2018). Unsurprisingly, the binder hydration is the primary reason behind the change in both short- and long-term mechanical properties of cementitious materials (Vazquez & Pique, 2016), such as the modulus of elasticity and compressive strength (Fall et al., 2010). As noted earlier, mixing the CPB with a superplasticizer causes some chemical and physical changes in the material, which requires further understanding under different temperatures. There are several research studies in the past on the influence of temperature on the mechanical strength of concrete that contains superplasticizer. In a study of cement-superplasticizer interactions in cementitious systems under different ambient temperatures, it was found out that there is an increase in the admixture requirement with a rise in the temperature (Griesser, 2002). In another study by Heikal et al. (2005), a polycarboxylate superplasticizer was identified to extend the setting times of a silica fume blended cement paste at 35ºC than at 20ºC, and this will, in turn, affect its mechanical behavior. Results from other similar studies show that superplasticizer-concretes behave differently under different curing temperatures (Ghafoori & Diawara, 2010; Kong & Sanjayan, 2010; Lukowski, 2016). Investigating such interactions with regard to CPB would be beneficial for its design and production. However, no study has been carried out so far on the coupled effects of curing temperature and curing time on the strength of CPB with superplasticizer.

Based on what has been highlighted above, this paper presents and discusses the findings from experimental research on the effects of curing time and temperature (2ºC, 20ºC and 35ºC) on the strength of CPB containing superplasticizer.

4.2. Experimental program

4.2.1. Materials used

4.2.1.1. Tailings

Two different types of tailings were used for the preparation of the specimens used in this study. They include natural tailings (NT) collected from a paste backfill plant located in the eastern part of Canada, and artificial silica tailings (ST), a product of U.S. Silica Co. Their physical properties are presented in Table 1 and the mineralogical compositions in Table 2. The ST, which constitutes about 99.8 wt.% quartz, is a pure ground silica powder with no reactive compounds. It serves as a controlled medium in order to minimize result uncertainties that may be caused by the chemical reaction associated with such compounds. The NT contains a wide range of minerals some of which are reactive (such as chlorite or pyrite) and may interact with the binder in the CPB. In addition, the pore water chemistry of the NT, as shown in Table 3 shows the presence of sulphate and other ions that are also reactive in CPB. To ensure that the water to cement ratio is constant, the natural water content of the NT was determined and then incorporated in the mixing water.

Table 4.1. Physical properties of the tailings

Property Unit	G_s -	D_{10} µm	D_{30} µm	D_{50} µm	D_{60} µm	D_{90} µm	% fine (<75µm)	S_s cm^2/g
ST	2.70	1.9	9.0	22.5	22.5	88.9	87.1	3600
NT	2.78	1.3	7.0	19.0	30.0	280.0	80.0	2491

Table 4.2. Mineralogical compositions of the tailings

Tailings/Mineral (wt.%)	Quartz	Albite	Chlorite	Muscovite	Biotite	Dolomite	Others	Total
ST	99.8						0.2	100
NT	26.1	21.3	11.4	26.3	2.7	11.3	0.9	100

Table 4.3. Pore water chemistry of the natural tailings

Tailings/ion (ppm)	Al	K	As	Ca	Si	Ni	Cu	Fe	Mg	Co	Mn	Sr	Na	S	So_4^{2-}
NT	<1	25.8	<300	455	1.8	448	<20	0.29	1130	264	3.93	1690	48.9	1770	5270

4.2.1.2. Binder and water

Portland cement type I (PCI) is used as the basic binding material for the preparation of the CPB used in the study. Also, fly ash (FA), and blast furnace slag (Slag) were added as partial replacements of the PCI. Table 4 presents the properties of all the three binders. Ordinary tap water was used for mixing the CPB ingredients.

Table 4.4. Physical and chemical properties of the binders

Binder Type	MgO (wt.%)	CaO (wt.%)	SiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	SO_3 (wt.%)	Relative Density	Specific surface area (cm^2/g)
PCI	2.65	62.82	18.03	4.53	2.70	3.82	3.1	1300
FA	5.58	21.47	38.06	19.45	5.33	2.7	2.6	2200

Slag	10.98	41.14	34.32	9.54	-	3.87	2.8	2100

4.2.1.3. Chemical admixture

Master Glenium 7500 produced by Badische Anilin und Soda Fabrik (BASF) is the superplasticizer used to prepare the CPB mixes. As a full range water reducing agent, it is largely used for the improvement of the workability of various cementitious materials used in the construction industry. The superplasticizer satisfies the ASTM standard C494/C494M for high-range water-reducing admixture (BASF 2015). For the CPB prepared in this study, the superplasticizer significantly improved the workability of the CPB as observed from the slump test according to ASTM Standard C143. The slump for 0%, 0.125%, and 0.25% were found to be 22.2 cm, 29.6 cm, and 29.8 cm respectively. The superplasticizer proportions were adopted to comply with the practice at the mine where the natural tailings were obtained.

4.2.2. Sample preparation and curing

Samples were prepared with varying proportions of binder and admixture contents to understand how each affects the mechanical strength of the CPB. Experimental program outlining the tests conducted is given in Table 5. The mixing, as well as curing temperature of all samples, was maintained at 2°C, 20°C and 35°C. For each CPB mix, the tailings material, binder, water and, when applicable, the admixture, were placed in a mechanical mixer located in a constant-temperature chamber and ran for about 7 minutes to achieve homogeneity. Pre-weighed ingredients were kept in the same chamber (an oven or a refrigerator, as the case may be) for a minimum of 24 hours to reach the designated temperature.

To prepare samples for UCS testing, airtight cylindrical moulds having a diameter of 5 cm and a height of 10 cm were used. Fresh CPB was poured into the moulds and gently agitated to remove air bubbles and then placed in the temperature-controlled chamber until testing.

Table 4.5. Summary of mix composition for specimens used

Sample Name	Tailings Type	Binder content (%)	PCI in the binder (%)	FA in the binder (%)	Slag in the binder (%)	W/C ratio	Superplasticizer content (%)	Curing Temperature (ºC)
Effect of superplasticizer on the UCS								
ST-0.0%	ST	4.5	100	0	0	7.35	0.0	2, 20, 35
ST-0.125%	ST	4.5	100	0	0	7.35	0.125	2, 20, 35
ST-0.25%	ST	4.5	100	0	0	7.35	0.25	2, 20, 3
Effect of binder type								
ST-PCI-100	ST	4.5	100	0	0	7.35	0.125	20
ST-PCI/FA-50:50	ST	4.5	50	50	0	7.35	0.125	20
ST-PCI/Slag-50:50	ST	4.5	50	0	50	7.35	0.125	20
Effect of tailings type								
ST-0.125%	ST	4.5	100	0	0	7.35	0.125	20
NT-0.125%	NT	4.5	100	0	0	7.35	0.125	20

PCI: Portland cement type I; FA: fly ash; ST: silica tailings; NT: natural tailings; W/C ratio: water to cement ratio by weight

4.2.3. Testing and monitoring of specimens

4.2.3.1. Unconfined compressive strength (UCS) test

The compressive strength of CPB specimens after curing periods of 1, 3, 7, and 28 days was determined in accordance with ASTM – C39. The test apparatus comprises an automated mechanical press having a loading rate set at 0.8 mm/min. The ultimate compressive stress at which the specimens fail was observed and recorded during the test. Each test was conducted at least 2 times to ensure the reproducibility of result.

4.2.3.2. Microstructural analyses

Multiple microstructural analysis tests were conducted to give information on the nature of the changes in the CPB due to binder reaction in the presence of the superplasticizer and at different curing conditions. These include thermal analyses (thermogravimetry/derivative thermogravimetry (TG/DTG)), mercury intrusion porosimetry (MIP) and X-ray diffraction (XRD). Cement pastes samples containing 0% and 0.125% admixture with a W/C ratio of 2 were prepared and then dried within an oven under 45ºC over a minimum of 4 days. Grounded specimens were then subjected to the TG/DTG analyses using a thermogravimetric analyzer, SDT 2960 simultaneous DSC-TGA. The test was performed under an N_2 atmosphere (100 mL/min) with a heating ramp of 10°C/min up to a maximum temperature of 1000°C. The XRD tests were conducted using Rigaku ultima IV diffractometer, a state-of-the-art system that is equipped with cross beam optics. The MIP was conducted on dried CPB specimens with a Micromeritics AutoPore III 9420 mercury porosimeter.

4.2.3.3. Monitoring program

The evolution of various properties in the CPB, namely electrical conductivity (EC), temperature, volumetric water content (VWC), and suction was monitored to shed more light on the hydration mechanism. The EC, VWC, and temperature were measured using a 5TE soil moisture sensor while an MPS-6 dielectric water potential sensor was used to determine the matric suction. Changes of the electrical conductivity in a cementitious material serve as a good indicator of the ionic transfer resulting from the chemical reactions taking place. The 5TE sensor has an accuracy of ±10% for the EC measurement; ±3% for the VWC; and ±1°C for the temperature. Likewise, the MPS-6 sensor has an accuracy of ±10% for a measurement range of –9 kPa to –100 kPa. Each monitoring device was inserted in the middle of a cylindrical mould having a diameter and height of 10 cm and 20 cm. Data was acquired using an EM50 data logger connected to a computer.

4.3. Results and discussions

4.3.1. Time dependent evolution of the strength of CPB containing superplasticizer

As illustrated in Fig. 1, there is a continuous improvement in mechanical strength for all the CPB samples made from both artificial and natural tailings from 1 day to 28 days curing time. For the ST, the lowest UCS for all the samples ranging from 102 kPa to 162 kPa occurred at day

1. After 28 days, the UCS increased considerably falling within the range of 352 kPa to 750 kPa. The samples made with NT exhibit a similar trend as shown in Fig. 2. Time-dependent strength achievement is associated with the amount of cement hydration products, e.g., portlandite (CH), ettringites and calcium silicate hydrate (C-S-H) in the material (Puertas et al. 2000; Tariq & Yanful, 2013; Jiang et al. 2017). It is consistent with the established fact on the dependence of the compressive strength of cementitious materials on the degree of hydration of the binder (Klemczak et al., 2016) as well as 70% of the binding effect in cement system being due to C-S-H (Richardson, 1999; Hawlett and Liska, 2019). Numerous established models link the hardening of concrete as well as other similar cementitious materials to the degree of cement hydration (e.g. De Schutter and Taerwe, 1995; Gutsch 2002; Schindler and Folliard, 2005). Generally, a stronger cemented matrix is formed due to the development of the hydration products which consequently strengthens the cohesion among the aggregate particles (Papadakis and Tsimas 2002; Puertas et al. 2000). In addition, the hydration reaction depletes the adsorbed water surrounding the aggregates and that leads to a further increase of inter-particle friction and, thus, the strength of the material (Hivon and Sego, 1995; Gmira et al., 2004). Several other studies performed on the mechanical strength of CPB are consistent with this observation (Huang et al., 2011; Yilmaz et al., 2014; Jiang and Fall, 2017). Fig. 1 and 2 also show that the CPB made from NT has less mechanical strength as compared to that made from pure silica tailings. The sulphate content (as shown in Table 3) in the natural tailings is responsible for the lower strength due to the capability of sulphate ions to inhibit cement hydration as demonstrated by previous research studies on the influence of sulphate ions on the compressive strength of CPB (Fall & Pokharel, 2010; Rong et al., 2017).

It is noticeable from Fig. 2 that the compressive strength of the NT-CPB containing 0.125% superplasticizer remain higher than that containing 0.25% superplasticizer up to 7 days. However, it became lower at 28 days curing time. In contrast, the improved strength due to higher superplasticizer content was observed after 3 days for the ST-CPB samples (Fig. 1). As it will be shown in section 3.7, superplasticizers have a retardation effect on the cement hydration, and thus the observed difference may be due to that. Furthermore, according to Zhang et al. (2015), the retardation behaviour of polycarboxylate superplasticizers largely defends on their charge characteristics. Considering that the NT used in this study contains several ions in the pore water (Table 3), the charges of the polymer chain in the superplasticizer may have been transformed thereby impacting the extent of the retardation effect.

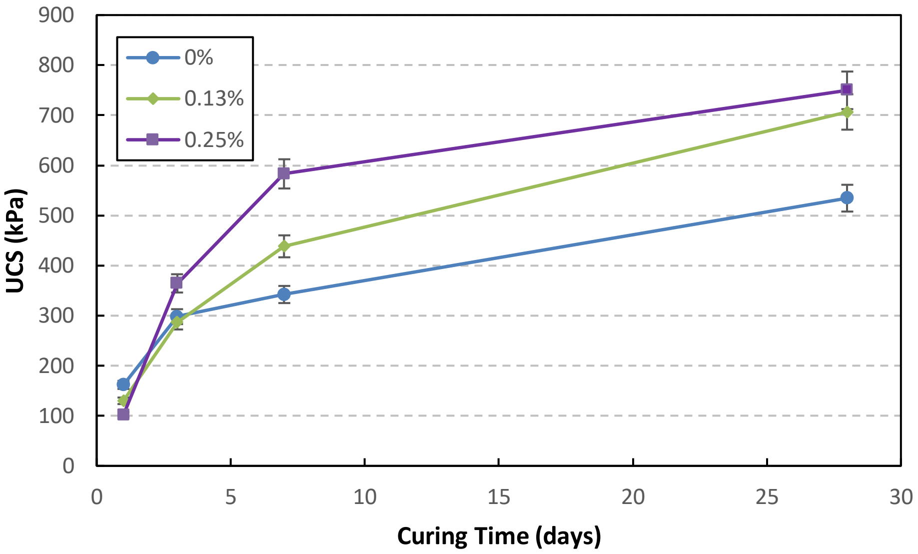


Figure 4.1. Unconfined compressive strength of ST-CPB with different superplasticizer contents at 20 ^{o}C

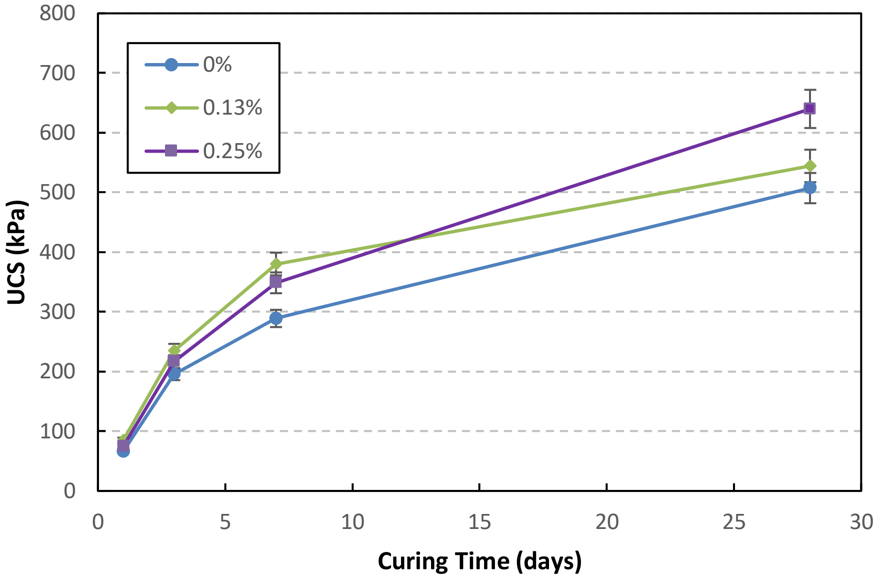


Figure 4.2. Unconfined compressive strength of NT-CPB with different superplasticizer contents at 20 ^{o}C

4.3.2 Effect of superplasticizer content on the strength development of CPB

Beside the consistent improvement with time, Fig. 1 and 2 also give information on the influence of the superplasticizer on the UCS of the CPB containing different dosages of superplasticizer. The CPB mixes containing 0.125% and 0.25% of the admixture exhibited compressive strength much higher than the CPB sample containing 0% starting from 7 days of curing. For the CPB made from ST, the 28 days UCS of 534 kPa increased to 706 kPa and 750 kPa with the addition of 0.125% and 0.25% superplasticizer, respectively. A similar trend is observed from the CPB made from natural tailings. This behavior can largely be attributed to the role played by superplasticizers on the cement hydration and particle mobility. When added to the CPB, the molecules of the polycarboxylate-based superplasticizer are adsorbed by the solid particles forming coated films that prevent flocculation (Duan et al., 2013; Bravo et al., 2017). As observed in other studies (e.g., Mollah et al., 2000; Puertas et al., 2005; Lothernbach and

Winnefeld, 2007), the cement particles in the material become dispersed by this process which leads to the retardation of their hydration in the early age. Unsurprisingly, Fig. 1 revealed that the early age strength (less than 7 days) of each of the CPB samples with superplasticizer is less than that of the CPB containing 0%. Evidence of this can be observed from the results of electrical conductivity and matric suction monitoring in the CPB samples shown in Fig. 3 and Fig. 4, respectively. An increase of electrical conductivity signifies increased flow of charge-carrying ions as a result of chemical reaction in the material (Morsy, 1999; Schwarz et al., 2007; Ercikdi et al., 2015). Thus, the change in the EC is a good parameter for assessing the nature of the cement hydration within the CPB. Although they both started from a similar value of about 3 mS/cm, the EC of the CPB without superplasticizer reached 4.5 mS/cm after 17 hours as opposed to just 3.67 mS/cm for the CPB containing 0.25%. This indicates that the CPB sample containing 0% superplasticizer exhibits faster cement hydration at an early age. Indeed, polycarboxylate-based superplasticizers such as the one used in this study are understood to retard the cement hydration of PCI during the first 30 hours (Lothenbach et al., 2007). However, the presence of the superplasticizer subsequently intensifies the cement hydration by favoring ionic diffusion (due to particle separation) at a later age (Puertas et al., 2005). Fig. 3 indicates that the EC in the 0.25% samples supersedes that of 0% after about 12 days curing onwards. This agrees with the matric suctions in the two samples (Fig. 4). The elevated chemical reaction from cement hydration leads to increased consumption of free water in the CPB containing 0.25% superplasticizer at a later age.

Furthermore, the TG/DTG diagrams in Fig. 5 give an insight on the hydration mechanism in the CPB under different admixture contents. The first peak on the DTG curve between 100^{o}C and 200^{o}C represents the sudden loss of weight due to the evaporation of capillary water and disintegration of the hydration products, e.g., ettringite, gypsum, carboaluminates, and C-S-H (Zou and Glasser, 2001; Haiqiang et al., 2016). The peak found between 400^{o}C and 500^{o}C is from the de-hydroxylation of calcium hydroxide (CH), while the third peak found between 650^{o}C and 750^{o}C is associated with the decomposition of calcite (Haiqiang et al., 2016). Comparing the TG/DTG curves of the 7-day cement paste containing 0% and 0.125% superplasticizer, the CPB sample containing 0.125% experienced the highest loss in the first and second peaks. This is an indication of more hydration products being produced in the presence of a higher percentage of the admixture content.

Another factor that plays a role in the improvement of the mechanical strength could be the self-consolidation of the solid particles in the CPB due to the dispersing effect of the admixture (Arezoumandi and Volz 2013; Li 2014; Haiqiang et al. 2016). Coupled with a larger amount of hydration products, this produces CPB with less pores and thus higher mechanical strength. The phenomenon is supported by the incremental porosity results from an MIP test on 7 days and 28 days CPB presented in Fig. 6. The results show that there is a high concentration of both small and large pores in the CPB without superplasticizer. The cumulative porosity in the CPB without superplasticizer is higher by about 10 percent at both curing ages. Increased porosity in CPB leads to lower mechanical strength (Li et al., 2015; Ke et al., 2017; Liu et al., 2018).

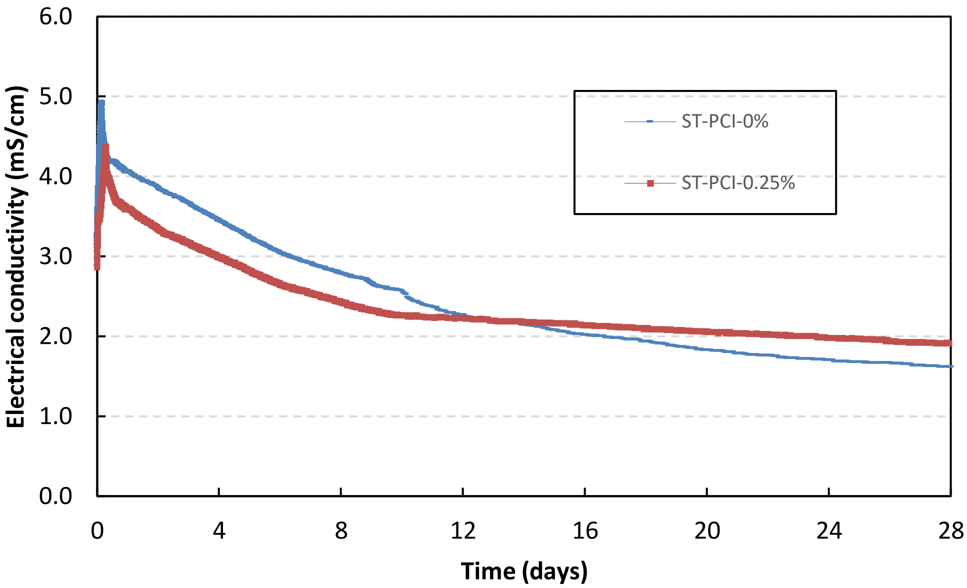


Figure 4.3. Evolution of EC in the CPB specimens with different superplasticizer contents

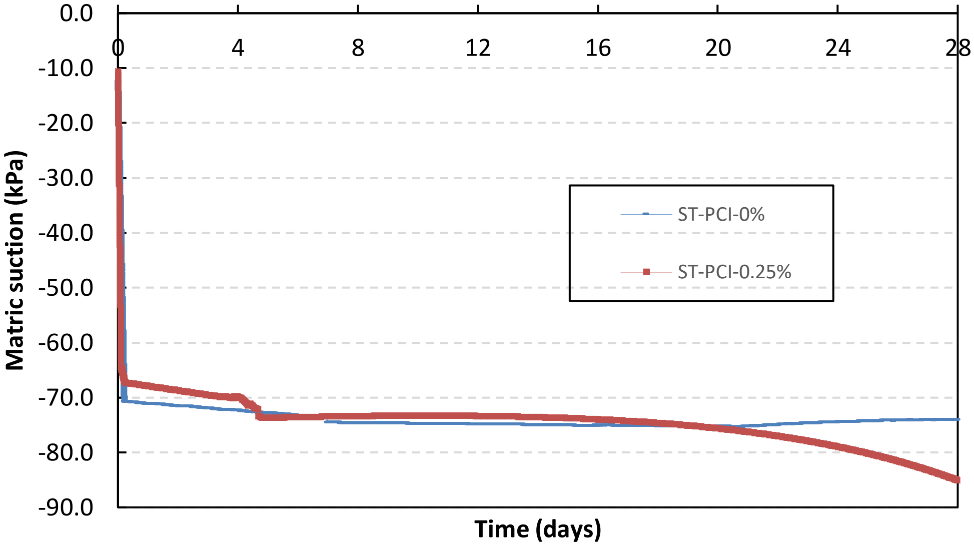


Figure 4.4. Evolution of suction in the CPB specimens with different superplasticizer contents

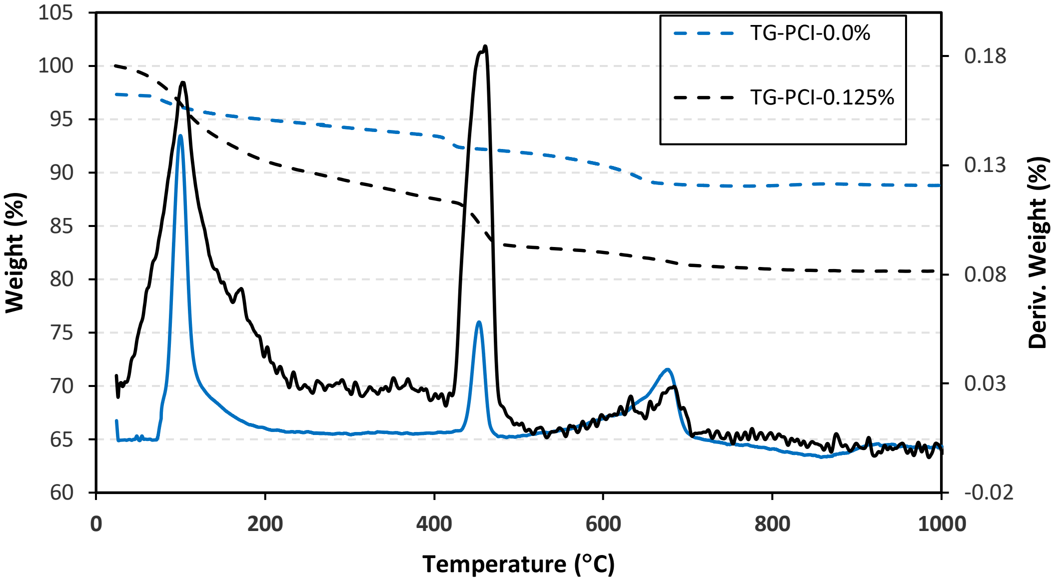
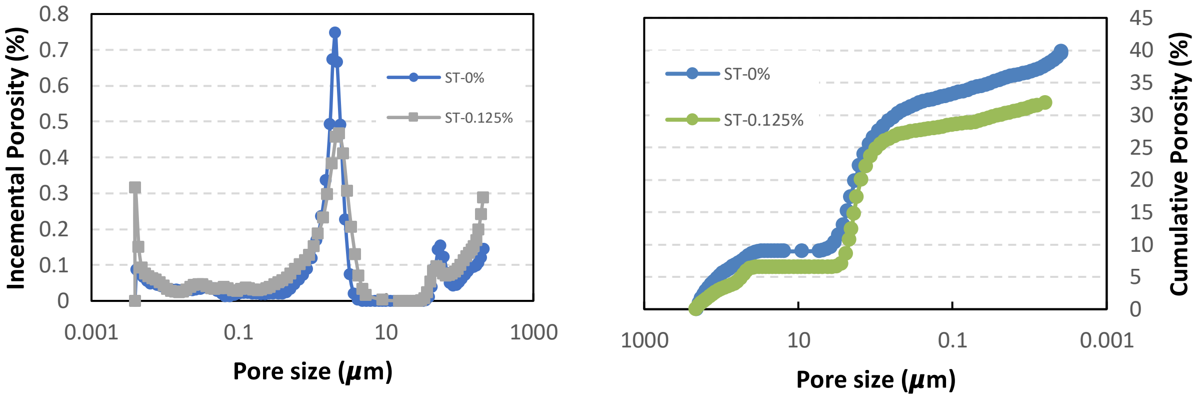
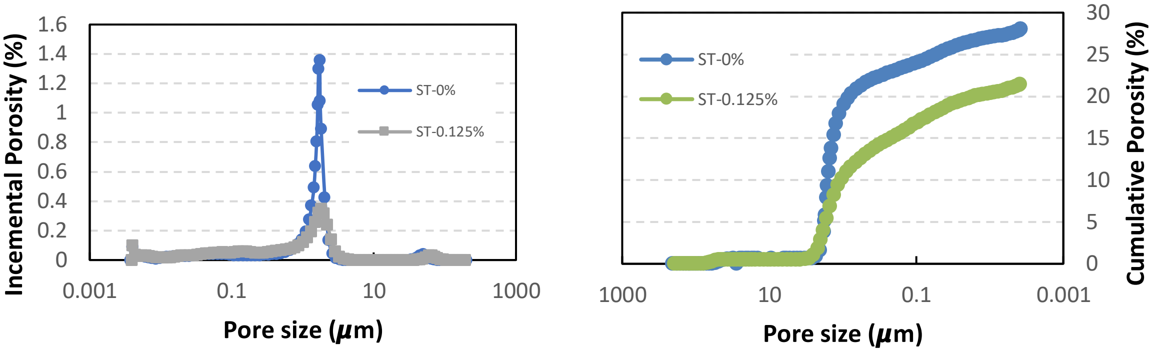


Figure 4.5. TG/DTG diagrams of 7-days cement pastes containing different superplasticizer contents



a) 7 days curing

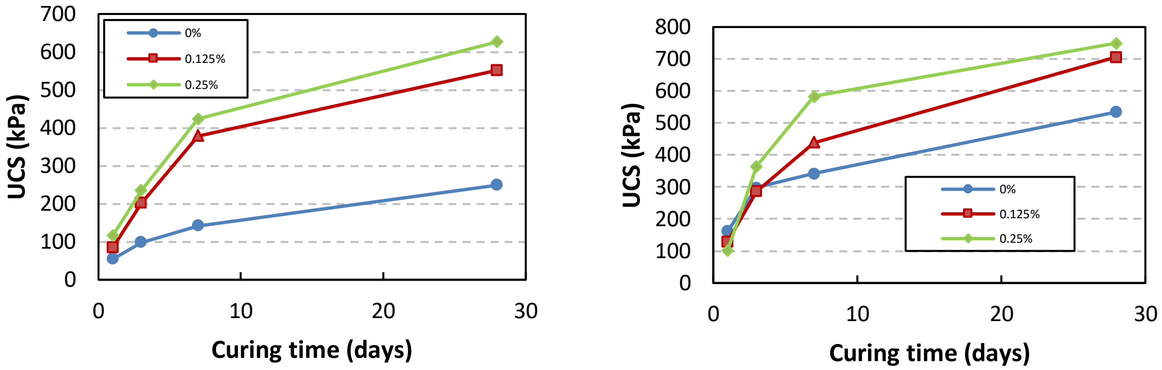


b) 28 days curing

Figure 4.6. Effect of superplasticizer on the pore size distribution and cumulative pore volume in the CPB samples

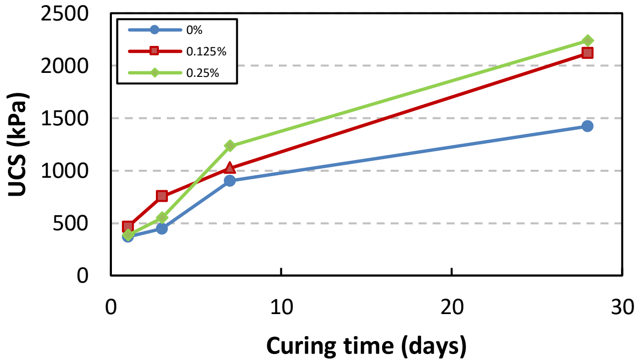
4.3.3 Temperature-dependent evolution of the strength of CPB containing superplasticizer

The experimental results presented in Fig. 7 indicate that the UCS of CPB is significantly influenced by temperature changes for all dosages of superplasticizer. Starting from 1 day curing time, the UCS is highest for the samples cured at 35^{o}C, followed by 20^{o}C and finally 2^{o}C curing temperature in all four cases. The difference is more pronounced by increasing the temperature above room temperature than by lowering it. Many studies on cementitious materials have established that an increase in temperature accelerates cement hydration (Kjellsen and Detwiler 1992; Escalante-Garcia 2003; Deschner et al., 2013). This is true even in the presence of a superplasticizer (Heikal et al., 2005). The increased rate of hydration generally leads to more hydration products being produced and consequently improving the binding forces between solid particles in the material (Lothenbach et al., 2007b). Fig. 8 presents the TG/DTG curves from a thermal analysis test on cement paste samples cured at 20^{o}C and 35^{o}C. It can be observed that both initial peaks in the DTG curve are higher for the 35^{o}C sample. Thus, more hydration products are produced at higher curing temperatures. Another interesting finding is the combined influence of superplasticizer and temperature on the compressive strength of the CPB. To understand this interaction more clearly, comparisons among the UCS curves for all the treatments at various curing temperatures are presented in Fig. 7. For each temperature, the UCS of CPB samples containing 0% superplasticizer exhibit the slowest increase with time. Thus, the temperature-induced increase in UCS is higher in CPB with superplasticizer than that without. Evidence of this interaction is better explained by the coupled processes in the CPB during the early age development that are discussed in Section 3.6.



a) 2 ^{o}C Curing temperature

b) 20 ^{o}C Curing temperature



c) 35 ^{o}C Curing temperature

Figure 4.7. Effect of superplasticizer on the strength of CPB cured at different temperatures

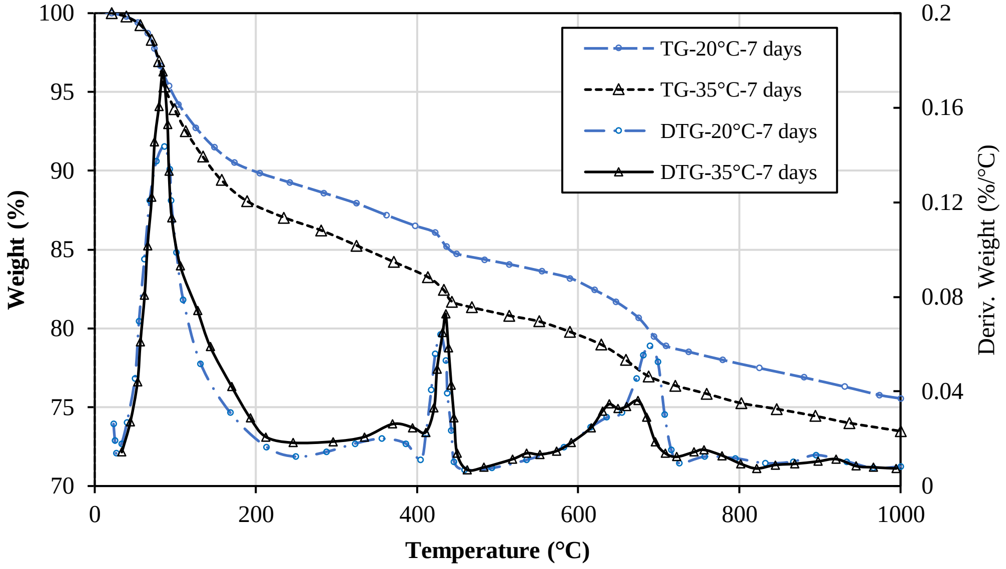


Figure 4.8. TG and DTG curves of 7-days cement paste with a curing temperature of 20°C and 35°C

4.3.4 Effect of binder type on the strength development of CPB with superplasticizer

The influence of cement replacement (50%) with FA and Slag in a CPB containing 0.125% superplasticizer on UCS is shown in Figures 9. The graphs indicate that the development of the compressive strength is a function of the binder composition used. Initially, the UCS of the three mixes show relatively similar compressive strength up to 7 days of curing, although the CPB containing 100% PCI slightly higher strength development than the other samples. However, only PCI/Slag sample has relatively similar UCS values to that of 100% PCI 689 kPa versus 706 kPa after 28 days as opposed to 545 kPa of the PCI/FA sample. This can be explained by the behavior of Slag and FA when used as a replacement for PCI. It has generally been reported that concrete containing Slag gains strength more slowly at an early age (due to the slow rate of hydration of Slag at early ages) but attain equal or higher strength at later stages (Bouzoubaa and Foo 2004). On the other hand, concrete containing FA is reported to exhibit slower strength gain than that containing Slag (due mainly to the slower rate of hydration of FA) as observed in this study (Li and Zhao 2003; Puertas et al. 2000; Thomas and Bamforth 1999; Swamy 1997). It is important to see that the superplasticizer did not inhibit the strength gain of the CPB even when the cement is partially replaced with lower-cost binders. A number of microstructural analyses tests on the samples highlight the differences based on the particle structures in the presence of the various binders and how they affect the strength development. The TG/DTG graphs given in Fig. 10 indicate that much more CH (the DTG peak at 400-500^{o}C) is produced in the 100% PCI samples. However, the PCI/Slag samples show the highest weight loss within the 100 – 200^{o}C interval which results from the decomposition of hydrates such as, ettringite, gypsum and C-S-H. In fact, Slag has been reported to improve the hydration of cement clinker by reacting with CH and consequently producing secondary C-S-H (Jiang and Fall, 2017). Elevated amounts of C-S-H and ettringite are noticeable in the PCI/Slag specimens during XRD analysis (Fig. 11). Further evidence of the binder type effect can be observed from the total porosity and pore distribution in the specimens given in Fig. 12. Majority of the pores in all the CPB specimens are have diameters around 0.05 µm, 2.0 µm,and 60.0 µ (represented by three peaks in Fig. 12 a) which is consistent with the pore-size distribution in the CPB from other studies (Fall & Samb2009; Aldhafeeri & Fall 2016). The CPB sample containing 100% PCI has the least total pore volume, and thus, expected to have the highest UCS values. Improvement of the mechanical strength of cementitious material containing slag and fly ash in the presence of superplasticizer has been observed by previous studies (e.g. Tan & Pu 1998; Brendt 2009; Parthiban 2013).

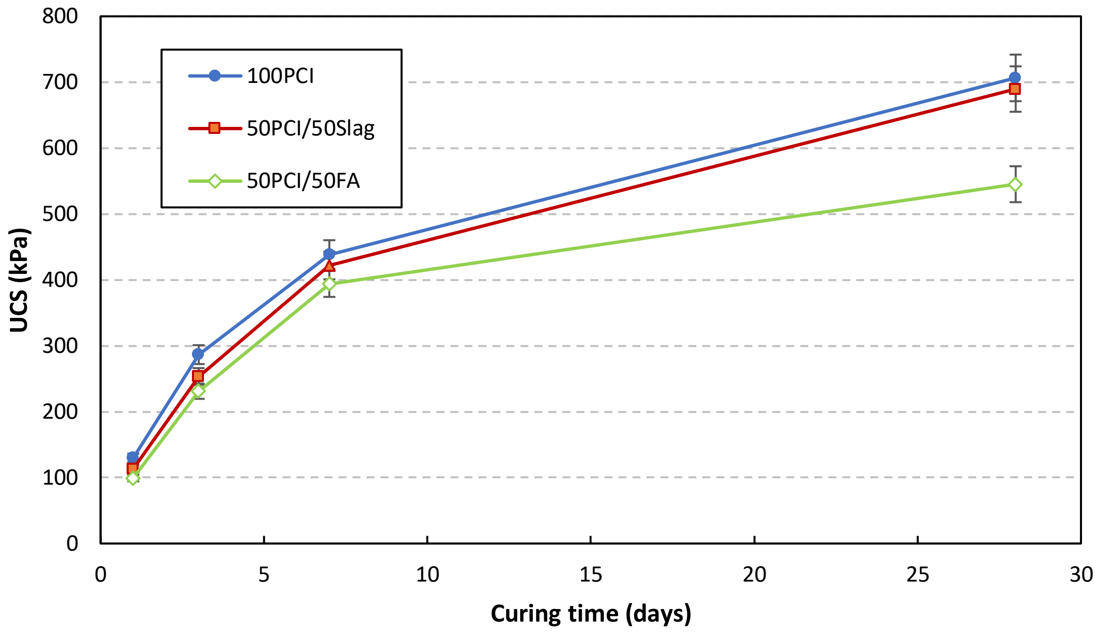


Figure 4.9. Effect of binder type on the strength of CPB containing superplasticizer

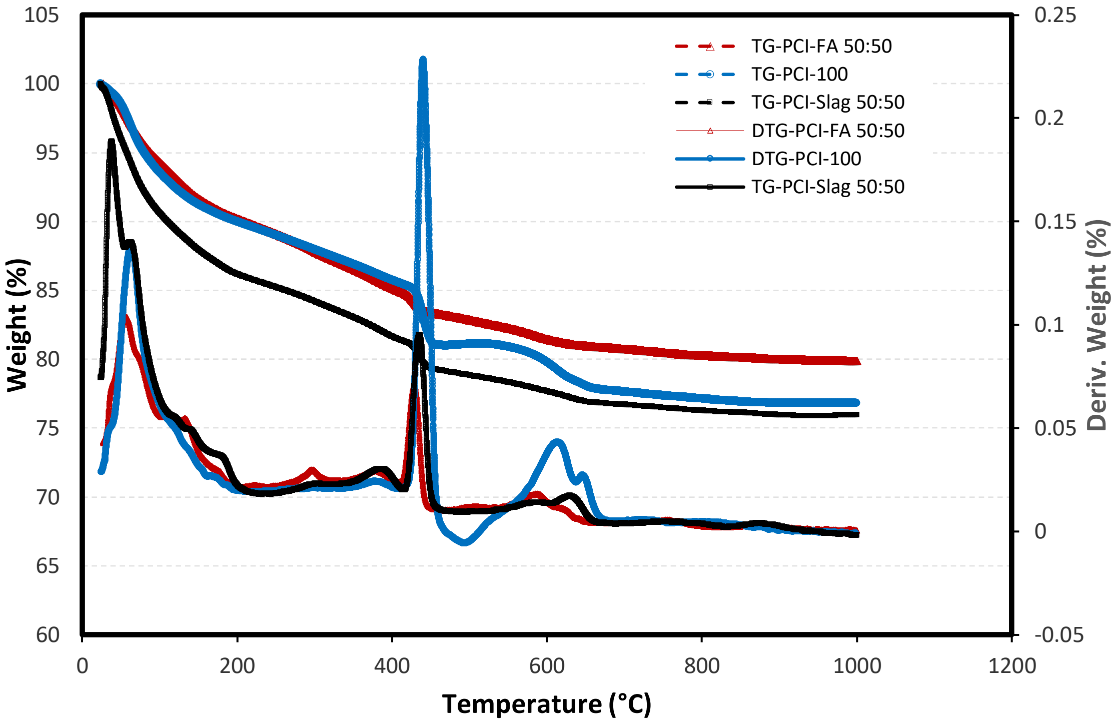
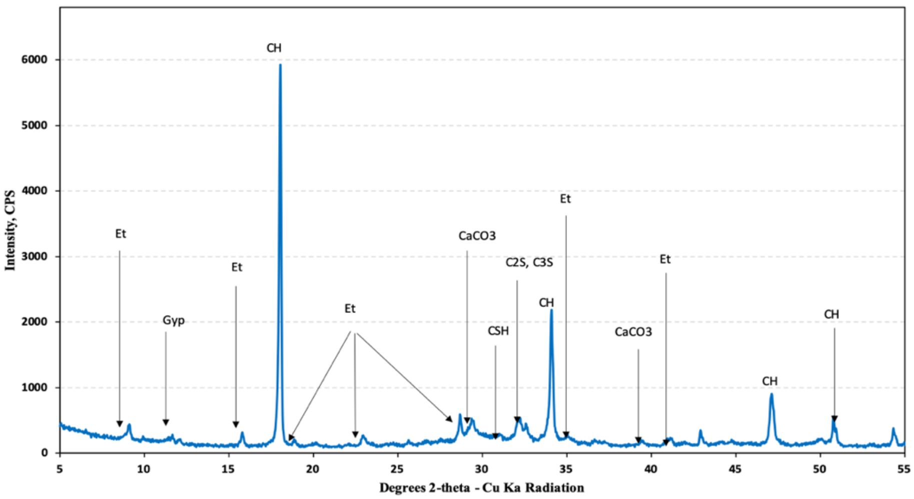
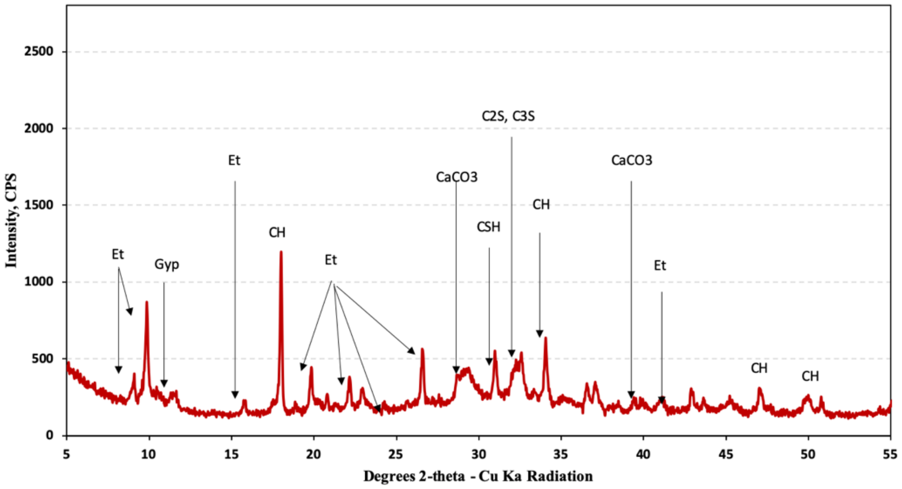


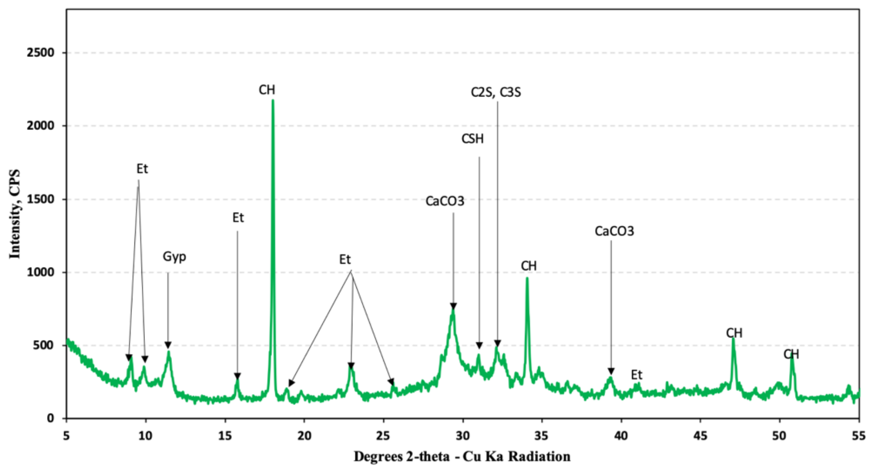
Figure 4.10. TG/DTG diagrams of 28-days pastes containing different binder types and 0.125% superplasticizer content



a) CPB containing 100% PCI

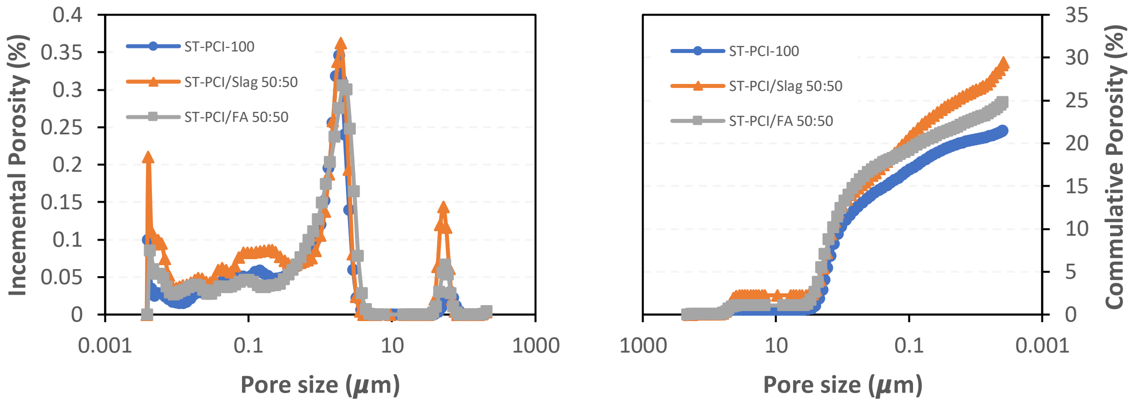


b) CPB containing 50:50 proportions of PCI and Slag



c) CPB containing 50:50 proportions of PCI and FA

Figure 4.11. XRD analysis result for 28 days cement paste containing different binder types

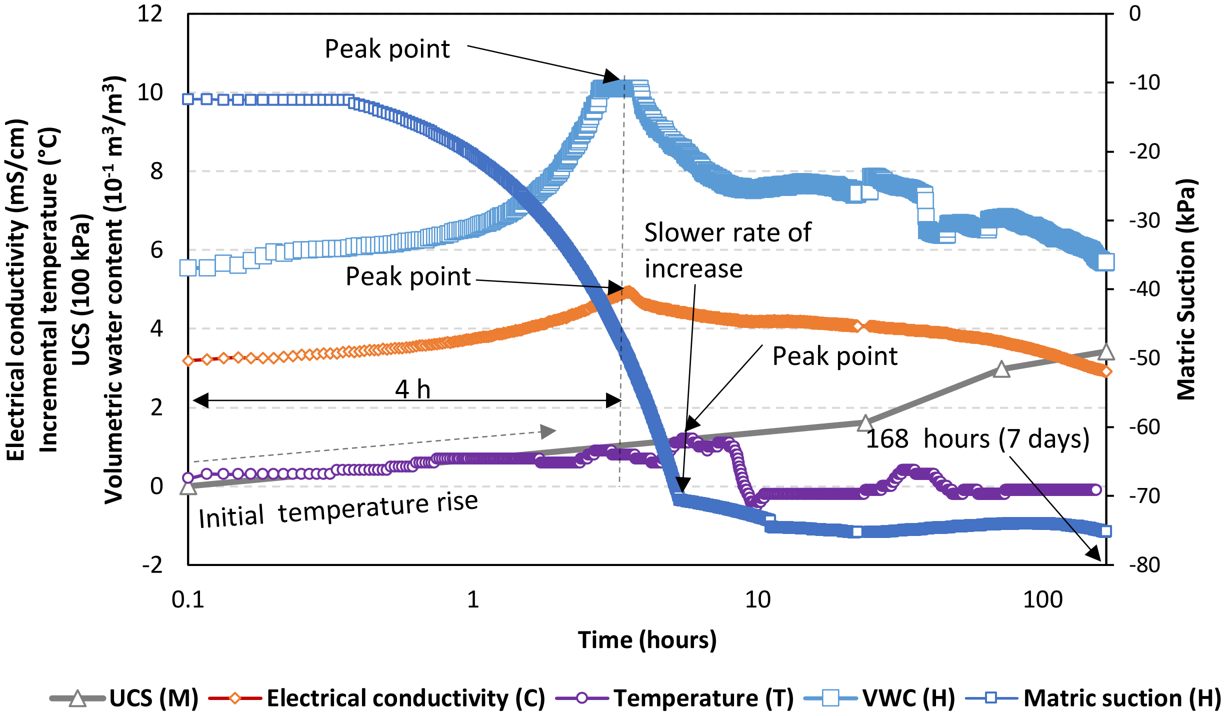


a) Pore distribution b) Cumulative pore volume

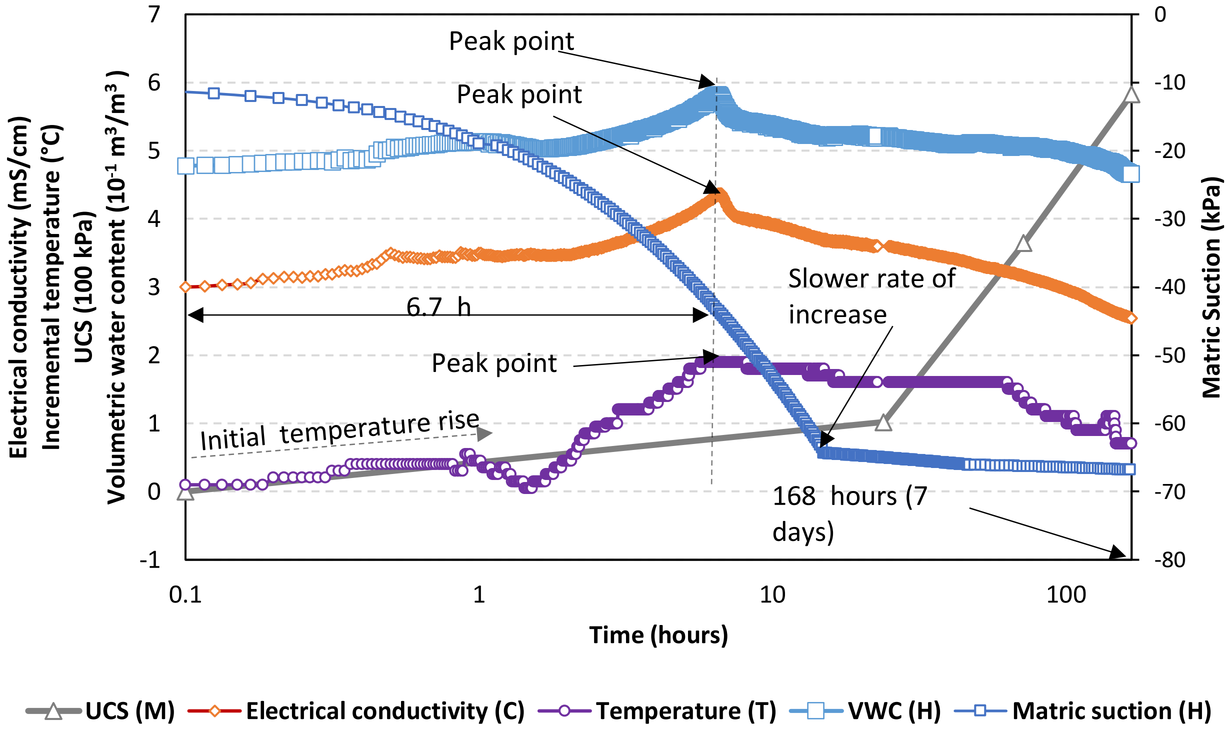
Figure 4.12. Effect of binder type on the pore size distribution and cumulative pore volume in the CPB samples cured for 28 days

4.3.6. Coupled THMC processes

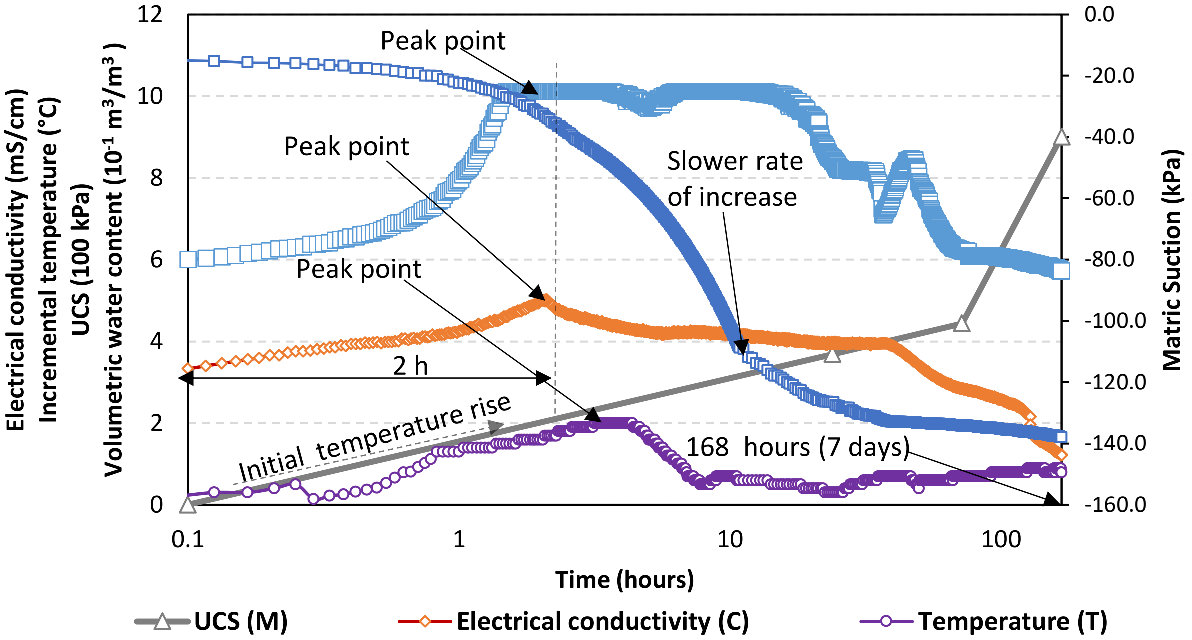
The changes in CPB and similar cementitious materials are mainly governed by the evolution of various processes, such as temperature (e.g. ambient temperature and heat of hydration), pore water pressure (positive or negative), chemical reactions (e.g. cement hydration), and mechanical strength (e.g. compressive strength). Either partially or combined, these factors have been extensively studied as part of the thermal (T), hydraulic (H), mechanical (M), and chemical (C) processes (Fall and Nasir, 2009; Maul et al., 2010; Cui and Fall, 2015; Wu et al., 2016). Fig. 13 presents the simultaneous evolution and interaction of these processes, namely temperature (T), matric suction and volumetric water content (H), UCS (M) and electrical conductivity (C) in the early curing age of CPB with and without superplasticizer at two different curing temperatures (20^{o}C and 35^{o}C). The matric suction represents the negative pore water pressure while the EC provides information on the advancement of the cement hydration. The figure shows that the THMC processes in CPB with or without superplasticizer appear to be interdependent. For the CPB samples containing 0% superplasticizer (cured at 20 and 35^{o}C), the incremental temperature began rising rapidly immediately after mixing and continued to increase to peak values of 1.80^{o}C and 1.99^{o}C after about 4 and 2 hours, respectively. The rise of temperature in fresh CPB is associated with the exothermic hydration reaction of the cement (Jansen et al., 2012). This corresponds to the changes of EC in the CPB, which also reached the peak values of 4.92 dS/cm and 5.0 dS/cm about the same time. The evolution of EC arises from ionic changes due to chemical reaction that is also linked to the cement hydration. Furthermore, there is a continuous increase in the negative pore water pressure throughout the curing period starting from -10 kPa and -15 kPa and subsequently reaching peak values -74 and -140 kPa in the samples cured at room temperature and 35^{o}C, respectively. The volumetric water content also began decreasing after the maximum temperature was attained. These hydraulic changes are also linked to the cement hydration which consumes the free water in the CPB (Li and Fall, 2016). It is noticeable that the rise of the matric suction slows down soon after the EC and temperature dropped. However, in the presence of superplasticizer (Fig 13 b and d), the incremental temperature and EC changes are significantly slower at the early age. For the temperature, peak values of 1.9^{o}C and 3.0^{o}C were attained after about 6.7 and 4 hours for the CPB samples cured at 20 and 35^{o}C, respectively. Corresponding EC peaks of 4.37 dS/cm and 3.77 dS/cm were attained over the same period. Thus, it can be noted that the time to reach the peak hydration rate, corresponding to the peak ET and temperature values is much longer than the usual time identified in CPB mixes without superplasticizer (Ghirian and Fall, 2015; Wang et al., 2016). The reason for the difference is the retardation of cement hydration by the superplasticizer at the early age, as discussed earlier. Furthermore, the evolution of the UCS largely corresponds to the three processes explained. For the 20^{o}C curing temperature, the 1-day (24 hours) UCS of the CPB without superplasticizer (160 kPa) is much higher than that of the CPB containing 0.25% superplasticizer (100 kPa). However, the CPB containing superplasticizer attained higher strength at both 3-days and 7-days curing time (72 and 168 hours) with UCS values of 364 kPa and 583 kPa as opposed to 297 kPa and 342 kPa for the CPB without superplasticizer. Thus, the initial retardation of hydration reaction by the superplasticizer and later improvement play an important role on the strength development of the CPB. At higher temperatures, the UCS for the CPB containing superplasticizer is higher starting from 1-day curing time. Possibly, the retardation of cement hydration (leading to lower strength at early age) is compensated by the acceleration due to elevated temperature. The revelation is of great significance in the backfilling process and the overall efficiency of the mining operation. Early strength development of the CPB ensures a self-supporting backfill that is required where free surfaces may be exposed by later mining (Thompson et al., 2012). Thus, containment barricades built at the mine stopes could be opened faster without high risks of failure (Yumlu and Guresci, 2007). Consequently, the use of superplasticizers under elevated temperatures would result in speeding up the mine cycles, which, in turn, would have a significant financial benefit for the mine.



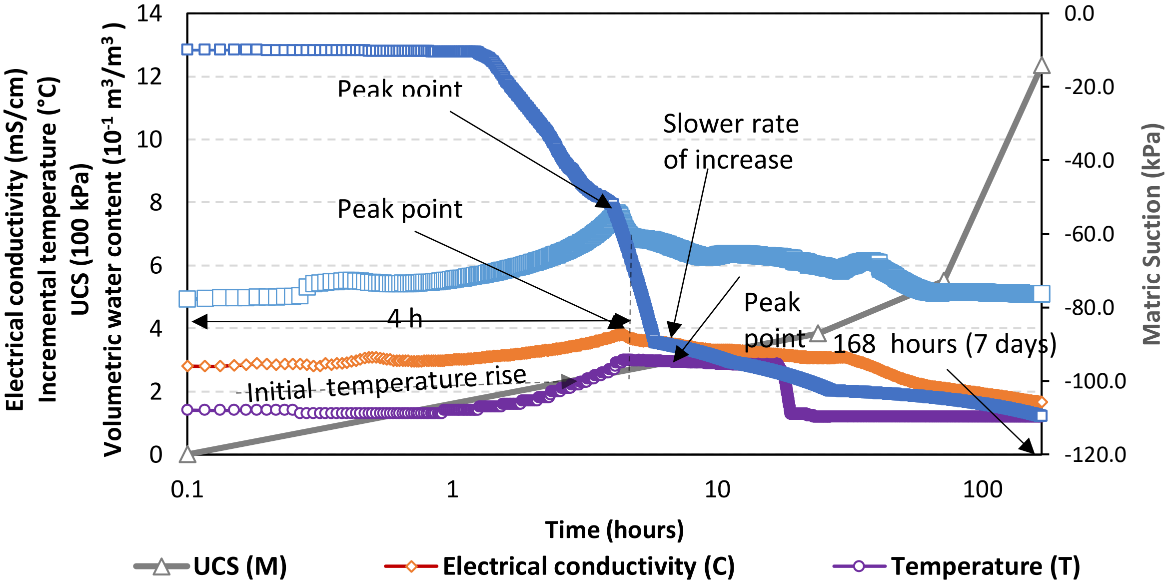
a) CPB sample with 0% superplasticizer cured at 20^{o}C



b) CPB sample with 0.25% superplasticizer cured at 20^{o}C



c) CPB sample with 0% superplasticizer cured at 35°C



d) CPB sample with 0.25% superplasticizer cured at 35°C

Figure 4.13. Coupled evolution of UCS, temperature, electrical conductivity and suction in CPB specimen containing superplasticizer

4.4. Summary and conclusions

This paper presents the findings from a study on the time- and temperature-dependent strength development of CPB samples containing different dosages of a polycarboxylate ether-based superplasticizer (0%, 0.05%, 0.125%, and 0.25%), binder type (Portland cement type I, fly ash, and slag), and tailings type (artificial and natural tailings). Different samples were prepared and cured for 1, 3, 7, and 28 days under three different ambient temperatures (2°C, 20°C, and 35°C). UCS tests were conducted on the samples to determine their compressive strength. Microstructural analyses (namely, thermogravimetry, XRD analysis, and mercury intrusion porosimetry) were also performed to understand the mechanisms responsible for the behaviors revealed by the results. Other tests include electrical conductivity, volumetric water content, temperature and matric suction monitoring. Based on that, the following conclusions can be made:

1. Increasing the admixture content to 0.125% and 0.25% results in a significant increase in the UCS as compared to the CPB without the superplasticizer. The improved strength is largely associated with the enhancement of cement hydration by the superplasticizer through ionic diffusion and self-consolidation of solid particles.
2. The temperature also plays a vital role on the strength development of the CPB. The compressive strength of all samples exhibits a sharp increase by changing the curing temperature in the order of 2°C > 20°C, > 35°C. It is noteworthy that the influence of the temperature on the strength is more noticeable in the CPB containing the superplasticizer. As revealed by the chemical and thermal behaviour of the cement hydration process, the reason lies in the shortening of the retardation of the hydration by the superplasticizer when temperature is increased.

3. The CPB made from natural tailings showed lower mechanical strength as compared to that made from pure silica tailings. The presence of sulphate ions in the natural tailings is responsible for the lower strength.
4. Partial replacement of the PCI with other binders, namely, fly ash and slag showed a decrease in the compressive strength. However, the decrease is very much less when 50% of the PCI is replaced with slag as compared to a significant reduction on replacement with fly ash.

Coupled thermal, hydraulic, mechanical, and chemical processes work together in the development of the mechanical strength of CPB containing superplasticizer.

4.5. References

Aldhafeeri, Z., & Fall, M. (2016). Time and damage induced changes in the chemical reactivity of cemented paste backfill. *Journal of Environmental Chemical Engineering*, *4*(4), 4038-4049.

Aldhafeeri, Z., Fall, M., Pokharel, M., & Pouramini, Z. (2016). Temperature dependence of the reactivity of cemented paste backfill. Applied Geochemistry, 72, 10–19.

Aleem, S. A. E., Heikal, M., & Morsi, W. M. (2014). Hydration characteristic, thermal expansion and microstructure of cement containing nano-silica. *Construction and Building Materials*, *59*, 151-160.

Arezoumandi, M., and Volz, J. S. 2013. Shear Strength of Chemically Based Self-Consolidating Concrete Beams: Fracture Mechanics Approach versus Modified Compression Field Theory. *Journal of Materials in Civil Engineering*,*26*(4), 713-720.

BASF. (2015). MasterGlenium 7500 Full-range water-reducing admixture. Web. https://www.master-builders-solutions.basf.us/en-us/products/concrete-admixtures/water-reducers/water-reducers-high-range/masterglenium-7500

Benzaazoua, M., Fall, M., & Belem, T. (2004). A contribution to understanding the hardening process of cemented pastefill. *Minerals engineering*, *17*(2), 141-152.

Björnström, J., & Chandra, S. (2003). Effect of superplasticizers on the rheological properties of cements. *Materials and Structures*, *36*(10), 685-692.

Bouzoubaa, N., & Foo, S. (2004). Use of fly ash and slag in concrete: A Best Practice Guide. *Materials and Technology Laboratory, MTL, 16.*

Bravo, M., de Brito, J., Evangelista, L., & Pacheco, J. (2017). Superplasticizer's efficiency on the mechanical properties of recycled aggregates concrete: Influence of recycled aggregates composition and incorporation ratio. *Construction and Building Materials*, *153*, 129-138.

Berndt, M. L. (2009). Properties of sustainable concrete containing fly ash, slag and recycled concrete aggregate. *Construction and building materials*, *23*(7), 2606-2613.

Cui, L., & Fall, M. (2015). A coupled thermo–hydro-mechanical–chemical model for underground cemented tailings backfill. *Tunnelling and Underground Space Technology*, *50*, 396-414.

Cui, L., & Fall, M. (2016). An evolutive elasto-plastic model for cemented paste backfill. *Computers and Geotechnics*, *71*, 19-29.

Deschner, F., Lothenbach, B., Winnefeld, F., & Neubauer, J. (2013). Effect of temperature on the hydration of Portland cement blended with siliceous fly ash. *Cement and concrete research*, *52*, 169-181.

De Schutter, G., & Taerwe, L. (1995). General hydration model for Portland cement and blast furnace slag cement. *Cement and Concrete Research*, *25*(3), 593-604.

Driussi, C., & Jansz, J. (2006). Technological options for waste minimization in the mining industry. *Journal of Cleaner production*, *14*(8), 682-688.

Duan, P., Shui, Z., Chen, W., & Shen, C. (2013). Influence of superplasticizer on composition and pore structure of C–S–H. *Construction and Building Materials*, *44*, 87-91.

Ercikdi, B., Külekci, G., & Yılmaz, T. (2015). Utilization of granulated marble wastes and waste bricks as mineral admixture in cemented paste backfill of sulphide-rich tailings. *Construction and Building Materials*, *93*, 573-583.

Escalante-Garcia, J. I. (2003). Nonevaporable water from neat OPC and replacement materials in composite cements hydrated at different temperatures. *Cement and Concrete Research*, *33*(11), 1883-1888.

Fall, M., Benzaazoua, M. and Saa, E.G., 2008. Mix proportioning of underground cemented tailings backfill. *Tunnelling and Underground space technology*, *23*(1), pp.80-90.

Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, *114*(3-4), 397-413.

Fall, M., & Nasir, O. (2009). Numerical modeling of the coupled thermo-chemo-mechanical response of cemented paste backfill structures in deep mine temperature conditions. In *Proceedings of the 3rd CANUS Rock Mechanics Symposium, Toronto, CD room*.

Fall, M., & Pokharel, M. (2010). Coupled effects of sulphate and temperature on the strength development of cemented tailings backfills: Portland cement-paste backfill. *Cement and Concrete Composites*, *32*(10), 819-828.

Fall, M., & Samb, S. S. (2009). Effect of high temperature on strength and microstructural properties of cemented paste backfill. *Fire Safety Journal*, *44*(4), 642-651.

Fang, K., & Fall, M. (2018). Effects of curing temperature on shear behaviour of cemented paste backfill-rock interface. *International Journal of Rock Mechanics and Mining Sciences*, *112*, 184-192.

Gelardi, G., & Flatt, R. J. (2016). Working mechanisms of water reducers and superplasticizers. In *Science and Technology of Concrete Admixtures* (pp. 257-278).

Ghafoori, N., & Diawara, H. (2010). Influence of temperature on fresh performance of self-consolidating concrete. *Construction and Building Materials*, *24*(6), 946-955.

Ghirian, A., & Fall, M. (2015). Coupled behavior of cemented paste backfill at early ages. *Geotechnical and Geological Engineering*, *33*(5), 1141-1166.

Gmira, A., Zabat, M., Pellenq, R. M., & Van Damme, H. (2004). Microscopic physical basis of the poromechanical behavior of cement-based materials. *Materials and Structures*, *37*(1), 3-14.

Gutsch, A. W. (2002). Properties of early age concrete-experiments and modelling. *Materials and Structures*, *35*(2), 76-79.

Hewlett, P., & Liska, M. (Eds.). (2019). *Lea's chemistry of cement and concrete*. Butterworth-Heinemann.

Heikal, M., Morsy, M. S., & Aiad, I. (2005). Effect of treatment temperature on the early hydration characteristics of superplasticized silica fume blended cement pastes. *Cement and Concrete Research*, *35*(4), 680-687.

Hivon, E. G., & Sego, D. C. (1995). Strength of frozen saline soils. *Canadian Geotechnical Journal*, *32*(2), 336-354.

Huang, S., Xia, K., & Qiao, L. (2011). Dynamic tests of cemented paste backfill: effects of strain rate, curing time, and cement content on compressive strength. *Journal of Materials Science*, *46*(15), 5165-5170.

Jansen, D., Goetz-Neunhoeffer, F., Lothenbach, B., & Neubauer, J. (2012). The early hydration of Ordinary Portland Cement (OPC): An approach comparing measured heat flow with calculated heat flow from QXRD. *Cement and Concrete Research*, *42*(1), 134-138.

Jiang, H., & Fall, M. (2017). Yield stress and strength of saline cemented tailings in sub-zero environments: Portland cement paste backfill. *International Journal of Mineral Processing*, *160*, 68-75.

Jiang, H., Fall, M., & Cui, L. (2017). Freezing behaviour of cemented paste backfill material in column experiments. *Construction and Building Materials*, *147*, 837-846.

Ke, B., Zhou, K., Deng, H., & Bin, F. (2017). NMR pore structure and dynamic characteristics of sandstone caused by ambient freeze-thaw action. *Shock and Vibration, 2017*.

Kjellsen, K. O., & Detwiler, R. J. (1992). Reaction kinetics of Portland cement mortars hydrated at different temperatures. *Cement and Concrete Research*, *22*(1), 112-120.

Klemczak, B., Batog, M., & Pilch, M. (2016). Assessment of concrete strength development models with regard to concretes with low clinker cements. *Archives of Civil and Mechanical Engineering*, *16*(2), 235-247.

Kong, D. L., & Sanjayan, J. G. (2010). Effect of elevated temperatures on geopolymer paste, mortar and concrete. Cement and concrete research, 40(2), 334-339.

Li, W., Fall, M. (2016). Sulphate effect on the early age strength and self-desiccation of cemented paste backfill. Journal of Construction and Building Materials 106: 296-304.

Li J. L., Zhou, K. P., & Ke., B. (2015). Association analysis of pore development characteristics and unconfined compressive strength property of granite under freezing-thawing cycles. Journal of *China Coal Society*, 40 (8), 1783-1789.

Li, W., 2014. *Dynamic segregation of self-consolidating concrete: new test method and effects of mix proportions* (Doctoral dissertation, [Honolulu]: [University of Hawaii at Manoa].

Li, G., & Zhao, X. (2003). Properties of concrete incorporating fly ash and ground granulated blast-furnace slag. *Cement and Concrete Composites*, *25*(3), 293-299.

Liu, L., Fang, Z., Qi, C., Zhang, B., Guo, L., & Song, K. I. (2018). Experimental investigation on the relationship between pore characteristics and unconfined compressive strength of cemented paste backfill. *Construction and Building Materials*, *179*, 254-264.

Lothenbach, B., Winnefeld, F., & Figi, R. (2007a). The influence of superplasticizers on the hydration of Portland cement. *Empa, Dübendorf, Switzerland*.

Lothenbach, B., Winnefeld, F., Alder, C., Wieland, E., & Lunk, P. (2007b). Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes. *Cement and Concrete Research*, *37*(4), 483-491.

Lukowski, P. (2016). Influence of temperature on efficiency of superplasticizing admixtures for concrete. *Journal of Building Chemistry*, *1*(1), 32-36.

Maul, P., Benbow, S., Bond, A., & Robinson, P. (2010). *Modelling Coupled Processes in the Evolution of Repository Engineered Barrier Systems using QPAC-EBS* (No. SSM--2010-25). Swedish Radiation Safety Authority.

McCarter, W. J., & Curran, P. N. (1984). The electrical response characteristics of setting cement paste. *Magazine of Concrete Research*, *36*(126), 42-49.

Mollah, M. Y. A., Adams, W. J., Schennach, R., & Cocke, D. L. (2000). A review of cement superplasticizer interactions and their models. *Advances in Cement Research*, *12*(4), 153-161.

Morsy, M. S. (1999). Effect of temperature on electrical conductivity of blended cement pastes. *Cement*

and concrete research, *29*(4), 603-606.

Naik, T. R., Kumar, R., Ramme, B. W., & Canpolat, F. (2012). Development of high-strength, economical self-consolidating concrete. *Construction and Building Materials*, *30*, 463-469.

Nasir, O., & Fall, M. (2010). Coupling binder hydration, temperature and compressive strength development of underground cemented paste backfill at early ages. *Tunnelling and Underground Space Technology*, *25*(1), 9-20.

Papadakis, V. G., & Tsimas, S. (2002). Supplementary cementing materials in concrete: Part I: efficiency and design. *Cement and concrete research*, *32*(10), 1525-1532.

Parthiban, K., Saravanarajamohan, K., Shobana, S., & Bhaskar, A. A. (2013). Effect of replacement of slag on the mechanical properties of fly ash based geopolymer concrete. *International Journal of Engineering and Technology (IJET)*, *5*(3), 2555-2559.

Pokharel M., Fall, M., (2010). Coupled thermo-chemical effects on the strength development on Slag-Paste backfill materials. ASCE Journal of Materials in Civil Engineering 23(5): 511-525.

Puertas, F., Martínez-Ramírez, S., Alonso, S., & Vazquez, T. (2000). Alkali-activated fly ash/slag cements: strength behaviour and hydration products. *Cement and Concrete Research*, *30*(10), 1625-1632.

Puertas, F., Santos, H., Palacios, M., & Martínez-Ramírez, S. (2005). Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes. *Advances in Cement Research*, *17*(2), 77-89.

Richardson, I. G. (1999). The nature of CSH in hardened cements. *Cement and concrete research*, *29*(8), 1131-1147.

Richardson, E., & Jordan, T. H. (2002). Seismicity in deep gold mines of South Africa: Implications for tectonic earthquakes. Bulletin of the Seismological Society of America, 92(5), 1766-1782.

Rico, M., Benito, G., Salgueiro, A. R., Díez-Herrero, A., & Pereira, H. G. (2008). Reported tailings dam failures: A review of the European incidents in the worldwide context. *Journal of hazardous materials*, *152*(2), 846-852.

Rong, H., Zhou, M., & Hou, H. (2017). Pore structure evolution and its effect on strength development of sulfate-containing cemented paste backfill. *Minerals*, *7*(1), 8.

Schindler, A. K., & Folliard, K. J. (2005). Heat of hydration models for cementitious materials. *ACI Materials Journal*, *102*(1), 24.

Schwarz, N., DuBois, M., & Neithalath, N. (2007). Electrical conductivity based characterization of plain and coarse glass powder modified cement pastes. *Cement and Concrete Composites*, *29*(9), 656-666.

Tan, K., & Pu, X. (1998). Strengthening effects of finely ground fly ash, granulated blast furnace slag, and their combination. *Cement and concrete research*, *28*(12), 1819-1825.

Tariq, A., & Yanful, E. K. (2013). A review of binders used in cemented paste tailings for underground and surface disposal practices. *Journal of environmental management*, *131*, 138-149.

Thompson, B. D., Bawden, W. F., & Grabinsky, M. W. (2012). In situ measurements of cemented paste backfill at the Cayeli Mine. *Canadian Geotechnical Journal*, *49*(7), 755-772.

Walske, M. L., McWilliam, H., Doherty, J., & Fourie, A. (2015). Influence of curing temperature and stress conditions on mechanical properties of cementing paste backfill. *Canadian Geotechnical Journal*, *53*(1), 148-161.

Wang, Y., Fall, M., & Wu, A. (2016). Initial temperature-dependence of strength development and self-desiccation in cemented paste backfill that contains sodium silicate. *Cement and Concrete Composites, 67*, 101-110.

Wu, D., Sun, G., & Liu, Y. (2016). Modeling the thermo-hydro-chemical behavior of cemented coal gangue-fly ash backfill. *Construction and Building Materials*, *111*, 522-528.

Wu, A., Wang, Y., Wang, H., Yin, S. and Miao, X., 2015. Coupled effects of cement type and water quality on the properties of cemented paste backfill. *International Journal of Mineral Processing*, *143*, pp.65-71.

Yahia, A., & Aïtcin, P. C. (2016). Self-consolidating concrete. In *Science and Technology of Concrete Admixtures* (pp. 491-502).

Yang, L., Yilmaz, E., Li, J., Liu, H., & Jiang, H. (2018). Effect of superplasticizer type and dosage on fluidity and strength behavior of cemented tailings backfill with different solid contents. *Construction and Building Materials*, *187*, 290-298.

Yilmaz, E., Belem, T., & Benzaazoua, M. (2014). Effects of curing and stress conditions on hydromechanical, geotechnical and geochemical properties of cemented paste backfill. *Engineering geology*, *168*, 23-37.

Yilmaz, E. (2011). Advances in reducing large volumes of environmentally harmful mine waste rocks and tailings. Gospodarka Surowcami Mineralnymi, 27(2), 89–112.

Yumlu, M., & Guresci, M. (2007). Paste backfill bulkhead monitoring-A case study from Inmet's Cayeli mine. In *Proceedings of the 9th International Symposium in Mining with Backfill (CD-ROM), Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, QC, Canada* (Vol. 29).

Zhang, Y. R., Kong, X. M., Lu, Z. B., Lu, Z. C., & Hou, S. S. (2015). Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes. *Cement and Concrete Research*, *67*, 184-196.

Chapter 5. Technical paper III – Insight into Saturated Hydraulic Conductivity of Cemented Paste Backfill Containing Polycarboxylate ether-based Superplasticizer

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Abstract

Recycling of tailings using cemented paste backfill (CPB) has become a popular practice in the mining industry in recent years. Superplasticizers are usually added to improve workability but there is a limited understanding of their influence on the properties of the CPB. Understanding the variations of the hydraulic conductivity of CPB containing polycarboxylate-based superplasticizer with different compositions and curing conditions is the main objective of this paper. The factors studied include: superplasticizer content of 0% and 0.125%; W/C ratios of 5, 7.35, and 10; three binders with proportions of 100% Portland Cement Type I (PCI), 50/50 PCI and blast furnace slag, 50/50 PCI and fly ash; sulphate content of 0 ppm and 25000 ppm. Samples were prepared and allowed to cure for 1, 7, 28, 60 and 90 days at 2°C, 20°C, and 35°C. Microstructural analyses were carried out to understand the principles behind the changes in hydraulic conductivity. It is found that the hydraulic conductivity decreases by the addition of superplasticizer. The reduction is largely attributable to the influence of the ether-based superplasticizer on particles mobility and cement hydration. Moreover, the findings indicate that both temperature and time have correlations with the hydraulic conductivity of CPB containing superplasticizer. Also, the presence of sulphate and partial replacement of PCI with blast furnace slag reduces the hydraulic conductivity. However, increasing the W/C ratio and replacement of PCI with fly ash results lead to the increase of the hydraulic conductivity. The variations are mainly due by changes in the CPB pore structure caused by the treatments.

Keywords: sustainable mining; tailings; cemented paste backfill; hydraulic conductivity; superplasticizer; valorization.

5.1 Introduction

Cemented paste backfill (CPB) offers an efficient means of mine waste (i.e. tailings) valorization both environmentally and economically. The tailings, which is the by-product of the milling process, are combined with a binder, water and chemical admixtures, when applicable, and used to fill the voids created from the mining. These mine tailings usually contain hazardous chemical compounds and would otherwise be impounded on the land posing a grave threat to the environment as well as human lives. In addition, the CPB technology is economically advantageous because it improves the productivity of ore retrieval during mining (Fridhonsson et al., 2013; Cui and Fall, 2016; Jiang et al. 2017). Moreover, binder inclusion ensures that the backfill becomes self-supporting after a short period making the excavation of adjacent ore body possible. To ensure optimal performance of CPB, its early-age and long-term behaviors have to be incorporated in the design (Wang et al., 2016). Some of these properties are responsible for its environmental performance (e.g. leachability and reactivity) and are largely associated with hydraulic conductivity (Abdul-Hussain & Fall, 2011; Grabinsky et al., 2008).

A notable environmental issue of great concern to the mining industry is the acid mine drainage (AMD). The term is used to describe the production of acidic water from sulfide-rich material when exposed to oxygen and water (Skousen et al., 2000; Akcil & Koldas, 2006). Although it occurs naturally, AMD is more prevalent across mining sites, whether operational or abandoned, due to increased exposure of sulphides by the mining operations (Simate & Ndlovu, 2014). This is because sulphide minerals occur as accessory minerals along with many other valuable minerals targeted by mining (Vaughan & Lennie, 1991; Gerasimov et al., 2019; Ren & Wang, 2019). In most cases, the sulphide compounds are inert due to the absence of molecular oxygen in the rock mass (Jacobs & Testa ,2014). Upon exposure to the atmosphere through mining, they react with oxygen and water to form sulfuric acid in the presence of acidophilic microorganisms (Jacobs & Testa, 2014). For example, oxidation of pyrite (FeS2 – a commonly occurring sulphide mineral) produces sulphuric acid as well as ferric iron under favorable conditions (Jennings et al., 2008). When produced in CPB, these compounds may leach into nearby groundwater body thereby leading to contamination.

Among the intrinsic properties of the CPB, hydraulic conductivity is the main parameter that governs the flow characteristics of the leachate or fluid (Fall et al., 2009a, b). A number of research studies conducted in recent years explored the hydraulic conductivity performance of CPB material (e.g. Belem et al., 2001; Godbout et al., 2007; Abdul-Hussain, 2011; Pokharel & Fall, 2013; Veenstra et al., 2014; Cihangir & Akyol, 2018). The variation of the hydraulic conductivity in the CPB has been attributed to different factors such as tailings fineness (Ke et al., 2016) binder content (Abdul-Hussain & Fall, 2011), binder types (Godbout et al., 2007; Ouellet et al., 2008), curing time and temperature (Yilmaz et al., 2010; Pokharel & Fall, 2013), and sulphate content (Wu et al., 2014; Pokharel & Fall, 2013). Nevertheless, none of the research studies investigated the effects of high range water reducing admixtures (superplasticizers) on the hydraulic conductivity of the CPB. Use of superplasticizers in CPB is being widely adopted in the mining industry, therefore understanding the nature of their influence on the key properties of the CPB is of paramount importance. Superplasticizers are added to CPB in order to improve its workability and/or flowability without exceeding required mixing water for optimal performance. These admixtures enhance the fluidity of cementitious materials owing to the characteristics of their organic polymer chains (Mollah & Adams, 2000). The soapy molecules of the superplasticizer coat the solid particles in the cementitious material causing dispersion by increasing the steric and electrostatic forces (Kauppi et al., 2005; Gelardi & Flatt, 2016). The major types of superplasticizers available commercially are made up of naphthalene, lignosulfonate, or polycarboxylate compounds (Björnström & Chandra, 2003; Bravo et al., 2017). The polycarboxylate-based superplasticizers are known to affect cement hydration reaction (Plank & Hirsch, 2007) and may behave differently in the presence of sulphide minerals (Pourchet et al., 2012; Pameijer, 2017) typically found in tailings. Despite these interactions, there has not been any scientific research to understand the hydraulic conductivity behavior of CPB containing this type of admixture.

In light of what is discussed above, the objective of this research paper is therefore to study the hydraulic conductivity behaviour of CPB admixed with polycarboxylate ether-based superplasticizer.

5.2 Materials and methods

5.2.1 Materials used

5.2.1.1 Tailings

Natural tailings (NT) and pure ground silica tailings (ST) were the main constituents of the CPB in this study. The NT was obtained from a gold mine in southern Ontario, Canada. With 99.8 wt% quartz and particle-size distribution (PSD) comparable to that of tailings from various mines in Canada (Figure 5.1), the ST is a good medium for laboratory experiments to minimize uncertainties. This is because it does not contain reactive minerals and, therefore, observed variation would be as a result of the treatments the CPB is subjected to. As shown in Figure 1, the ST contains about 45 wt.% fines (i.e. diameter < 20 μm), thus it can be categorized as medium tailings. On the other hand, the NT contains several chemical compounds such as albite and pyrite, as shown in Table 5.2. It was incorporated in the study to have a better understanding of the practicability of the tests since it is a better representation of the tailings used in practice. The percentage of the fines in the NT is about 36 wt.%, so it is also classified as medium tailings. To maintain uniform proportion of water in the CPB, the natural water content in the NT was calculated and integrated into the mass of the mixing water.

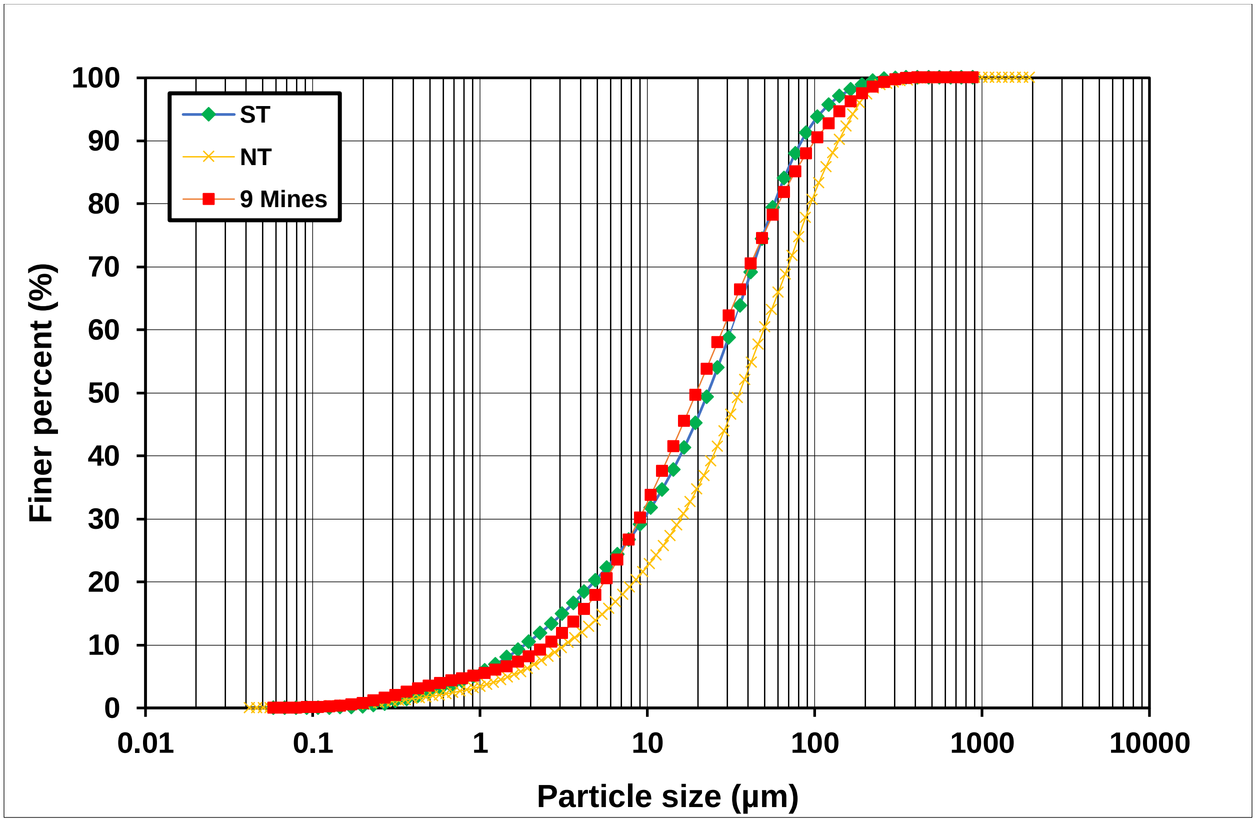


Figure 5.1. The PSD of the tailings used in this research with an average PSD of tailings from of 9 mines in Canada (PSD determined using laser particle size distribution analyzer)

Table 5.1. Physical properties of the artificial and natural tailings

Material	Property				
	D_{10} (µm)	D_{30} (µm)	D_{50} (µm)	D_{60} (µm)	Specific gravity (G_s)
NT	3.2	15.8	35.5	49.5	3.1
ST	1.9	9.0	22.5	31.5	2.7

Table 5.2. Mineralogy of the tailings (determined by XRD analysis)

Tailings	Mineral												
	Quartz	Albite	Chlorite	Dolomite	Talc	Calcite	Magnetite	Pyrrhotite	Spinel	Pyrite	Pyrrhotite	Others	Total
ST (w_t%)	99.8	-	-	-	-	-	-	-	-	-	-	0.2	100
NT (w_t%)	15	32.8	16.1	15	7	4.2	2.4	1.8	1.8	1	0.3	2.6	100

5.2.1.2 Binders

The main binder used in the study is the ordinary Portland cement type I (PCI). Because it accounts for a large portion of the CPB production cost, alternative pozzolans are often used as a replacement. For that reason, tests were conducted on CPB with part of the PCI replaced with fly ash (FA) and ground blast furnace slag (BFS) at a blending ratio of 50/50. The properties of the three binders are given in Table 5.3.

Table 5.3. Physical and chemical properties of the binders

Binder Type	MgO (wt.%)	CaO (wt.%)	SiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	SO_3 (wt.%)	Relative Density	Specific surface area (cm^2/g)
PCI	2.7	62.8	18.0	4.5	2.7	3.8	3.1	1300
FA	5.6	21.5	38.0	19.5	5.3	2.7	2.6	2200
BFS	11.0	41.1	34.3	9.5	-	3.9	2.8	2100

5.2.1.3 Chemical admixture

A polycarboxylate ether-based Superplasticizer, Master Glenium 7500, made by Badische Anilin und Soda Fabrik (BASF) was added as the water reducing admixture in the CPB samples preparation. The admixture is commonly used for improving the workability and/or flowability of concrete and similar construction materials. According to BASF (2015), the superplasticizer complies with the ASTM C494/C494M standard for high-range water reducers. The slump (determined according to ASTM C143/C143M-15a) of the CPB with 0% and 0.125% of the superplasticizer were respectively found to be 22.2 cm and 29.6 cm. The proportion used was chosen based on common practice in Canada.

5.2.1.4. Mixing Water

Ordinary tap water was used for mixing the constituents of the CPB. When admixture and/or sulphate are to be added, an appropriate mass was dissolved in the water before being added to the solids.

5.2.2. Preparation and curing of specimens

Specimens containing tailings and different compositions of superplasticizer, binders, sulphate, and water to cement ratio were prepared based on the experimental plan given in Table

5.4. For each mixture, the solids (i.e. tailings and binders) were first blended in a mechanical mixer for about 2 minutes after which the water containing the admixture and/or sulphate was added. The materials were then mixed further for an additional 5 minutes to achieve homogeneity. It is important to mention that the ingredients were always pre-weighed and kept in a temperature-controlled chamber (an oven or a refrigerator) over a period of at least 24 hours to achieve the desired temperature. Also, the same chamber was used during the mixing phase. Prepared CPB was then cast into 5 cm diameter by 10 cm height cylindrical moulds and agitated gently to remove air with the CPB. The moulds were t tightly sealed and kept in a temperature-control environment before testing. The specimens were cured for 1, 7, 28, 60, and 90 days.

5.2.3. Hydraulic conductivity test

The saturated hydraulic conductivity of cured CPB specimens was determined using Tri-Flex 2 flexible wall permeameter in compliance with ASTM standard D5084-16 standard. A constant head method was adopted with a pressure difference between the inflow and outflow being 10 Psi (69 kPa). Full saturation was achieved prior to the test by applying backpressure after bridging the inflow and outflow burettes until the flow through the specimen becomes constant. The tests were repeated at least two times to ensure reproducibility.

Table 5.4. Experimental plan showing the composition of CPB samples

Sample Name	Tailings Type	Binder content (%)	PCI in the binder (%)	FA in the binder (%)	BFS in the binder (%)	W/C ratio	Superplasticizer content (%)	Sulphate content (ppm)	Curing Temperature (^{o}C)
A. Time-dependent evolution of hydraulic conductivity									
CPB-ST-0.0%	ST	4.5	100	0	0	7.35	0.0	0	20
CPB-ST-0.125%	ST	4.5	100	0	0	7.35	0.125	0	20
CPB-NT-0.125%	NT	4.5	100	0	0	7.35	0.125	0	20
B. Effect of curing temperature on hydraulic conductivity									
CPB-0.125-Tem 2	ST	4.5	100	0	0	7.35	0.125	0	2
CPB-0.125-Tem 20	ST	4.5	100	0	0	7.35	0.125	0	20
CPB-0.125-Tem 35	NT	4.5	100	0	0	7.35	0.125	0	35
C. Effect of binder type on the hydraulic conductivity									
CPB-0.125-PCI	ST	4.5	100	0	0	7.35	0.125	0	20
CPB-0.125-PCI/FA	ST	4.5	50	50	0	7.35	0.125	0	20
CPB-0.125-PCI/BFS	ST	4.5	50	0	50	7.35	0.125	0	20
D. Effect of W/C ratio on the hydraulic conductivity									
CPB-0.125-W/C 5	ST	4.5	100	0	0	5	0.125	0	20
CPB-0.125-W/C 7.35	St	4.5	100	0	0	7.35	0.125	0	20
CPB-0.125-W/C 10	ST	4.5	100	0	0	10	0.125	0	20
E. Effect of sulphate on the hydraulic conductivity									
CPB-0.0-0 ppm	ST	4.5	100	0	0	7.35	0.0	0	20
CPB-0.0-2500 ppm	ST	4.5	100	0	0	7.35	0.0	2500	20
CPB-0.125-0 ppm	ST	4.5	100	0	0	7.35	0.125	0	20
CPB-0.125-25000 ppm	ST	4.5	100	0	0	7.35	0.125	2500	20

ST: artificial silica tailings; PCI: Portland cement type I; FA: fly ash; BFS: blast furnace slag; NT: natural tailings; W/C ratio: weight ratio of water to binder; ppm: parts per million

5.2.4. Microstructural analyses

Additional tests were carried out to understand the microstructural composition of the CPB with different treatments, namely thermogravimetric analysis (TG)/differential thermogravimetric (DTG) analysis, X-ray diffraction (XRD) analysis and mercury intrusion porosimetry (MIP). The TG/DTG and XRD tests were carried out on cement paste prepared with a W/C ratio of 2 (to provide sufficient water similar to that in CPB). The cement paste samples were prepared in the same manner and condition as the CPB specimens. After reaching the desired curing period, the specimens were oven-dried under 45^{o}C temperature until the mass becomes constant. The fully dried specimens were ground and analyzed accordingly. Thermogravimetric analyzer, SDT 2960 simultaneous DSC-TGA device was used for the TG/DTG test under a nitrogen atmosphere and heating ramp of 10^{o}C/min to a maximum temperature of 1000^{o}C. The XRD test was carried out using Rigaku ultima IV diffractometer equipped with cross beam optics at a scanning rate of 1 degree per minute. In contrast, the MIP test was carried out on CPB specimens that were also oven-dried at 45^{o}C temperature. Micromeritics AutoPore III 9420 mercury porosimeter was used.

5.3 Results and discussions

5.3.1 Time-dependent evolution of hydraulic conductivity of CPB

There is a consistent decrease in the hydraulic conductivity for all samples over the curing period regardless of the tailings type and the superplasticizer content as observed from Figure 5.2. The time-dependent variation of the hydraulic conductivity largely associated with the progression of cement hydration. Generally, the cement continues to undergo a chemical reaction in the presence of water leading to the production of compounds (such as ettringite, CSH, CH) that modify the pore structure of the CPB (Bullard et al., 2011; Marchon & Flatt, 2016; Li and Fall, 2028). In effect, the spaces in the material shrink as a due to the refinement and that would make the CPB less permeable. This can be noticed from the MIP graphs showing the distribution of pores in CPB specimens tested at different curing ages (Figure 5.3). Both incremental porosity and total pore volume are much higher in the CPB cured for 7 days. To further confirm the difference in the hydration products, cement paste samples with different curing times were subjected to thermal analyses. The 7 days and 28 days TG/DTG graphs presented in Figure 5.4. The DTG graphs exhibit three distinct peaks corresponding to the proportion of the hydration products that decompose within specific temperature ranges. The first peak occurs between 100^{o}C and 200^{o}C and it is caused by the dehydration of hydrates, (ettringite, gypsum, CSH) (Alonso & Fernandez, 2004; Pane and Hansen, 2005). The second peak (between 400^{o}C and 500^{o}C) is mainly as a result of the de-hydroxylation of portlandite (CH). The third peak (which is between 650^{o}C and 750^{o}C) is due to the decomposition of carbonated compounds as well as calcite (Zou and Glasser, 2001; Gabrovšek et al., 2006; Piqué et al., 2011; Li and Fall, 2018). The DTG graphs from Figure 5.4 indicate the presence of larger amount of hydration products (especially CH) for 28 days specimen than the 7 days specimen. This is reflected in the TG curves as there was about 80% of the 7 days specimen remaining after reaching 1000^{o}C temperature as opposed to 70% of the 28 days specimen. The reduction of hydraulic conductivity of CPB based on the progress of binderhydration has also been observed by other studies (Belem et al., 2001; Ouellet et al., 2008; Fall et al., 2009; Ghirian & Fall, 2015).

Beside the effect of curing time, Figure 5.2 also reveals that the hydraulic conductivity decreases by the replacement of ST with NT and by the addition of superplasticizer. The CPB-ST-0% sample has hydraulic conductivity values of 3.25E-5 cm/s and 2.68E-6 cm/s after 1 day and 90 days respectively, while the CPB-ST-0.125% sample 1.01E-5 cm/s and 1.51E-6 cm/s after the same curing period. The reduction can largely be attributed to the influence of the superplasticizer on particles mobility and cement hydration. When used in cementitious materials, polycarboxylate-based superplasticizer molecules form coated films around the solid particles thereby preventing flocculation (Fernandez-Alvarez et al., 2013; Zhang et al., 2016; Bravo et al., 2017; Haruna and Fall, 2020). Although this has been linked to the retardation of binder hydration reaction within few hours after mixing (Lothenbach, 2007; Zhang et al., 2015), the superplasticizer later amplifies the hydration through ionic diffusion and nucleation of hydrates as time passes (Puertas et al., 2005; He et al., 2019; Haruna and Fall, 2020). This claim is corroborated by the TG/DTG graphs of samples containing 0% and 0.125% superplasticizer cured for 7 days as shown in Figure 5.5. It is evident that much more hydration products are present in the specimen containing superplasticizer as it exhibits higher peaks. In addition to that, the dispersion of the solid particles by the superplasticizer also results in more intact structure due to self-consolidation (Arezoumandi and Volz 2013; Zhang & Kong, 2014; Vakhsouri & Nejadi, 2017). This will subsequently produce a CPB with less porosity and, therefore, less hydraulic conductivity as observed from the experimental results. The observation is supported by the MIP analysis on CPB samples containing 0% and 0.125% superplasticizer (Figure 5.6). The concentration of both coarse and fine pores is lower in the CPB containing superplasticizer. With respect to the tailings types, it is observed that the hydraulic conductivity of specimens made of NT is significantly lower than that made of ST in the early age (1 day and 7 days). Beyond 28 days of curing, there is relatively little or no difference between the hydraulic conductivity values. Because the two tailings have similar grain size distribution, the variation is likely associated with the mineralogical and chemical compositions. While the ST is completely nonreactive, the NT contains sulphide minerals, namely pyrite, Pyrrhotite and Pyrrhotite (Table 5.2) as well as other minerals and sulphate ions that could influence the cement hydration. The sulphide minerals in the tailings produce sulphate compounds in the presence of oxygen and water (Elberling & Nicholson, 1996; Tariq & Mehdi, 2007; Aldhafeeri et al. 2016). The effect of sulphates on the cement hydration will be explained in section 5.3.5. Also, there is a high percentage of chlorite in the NT (16.1%) and many forms of these minerals are known to be expansive, capable of preserving permeability (Silvester et al.,2011; Kennedy, 2015).

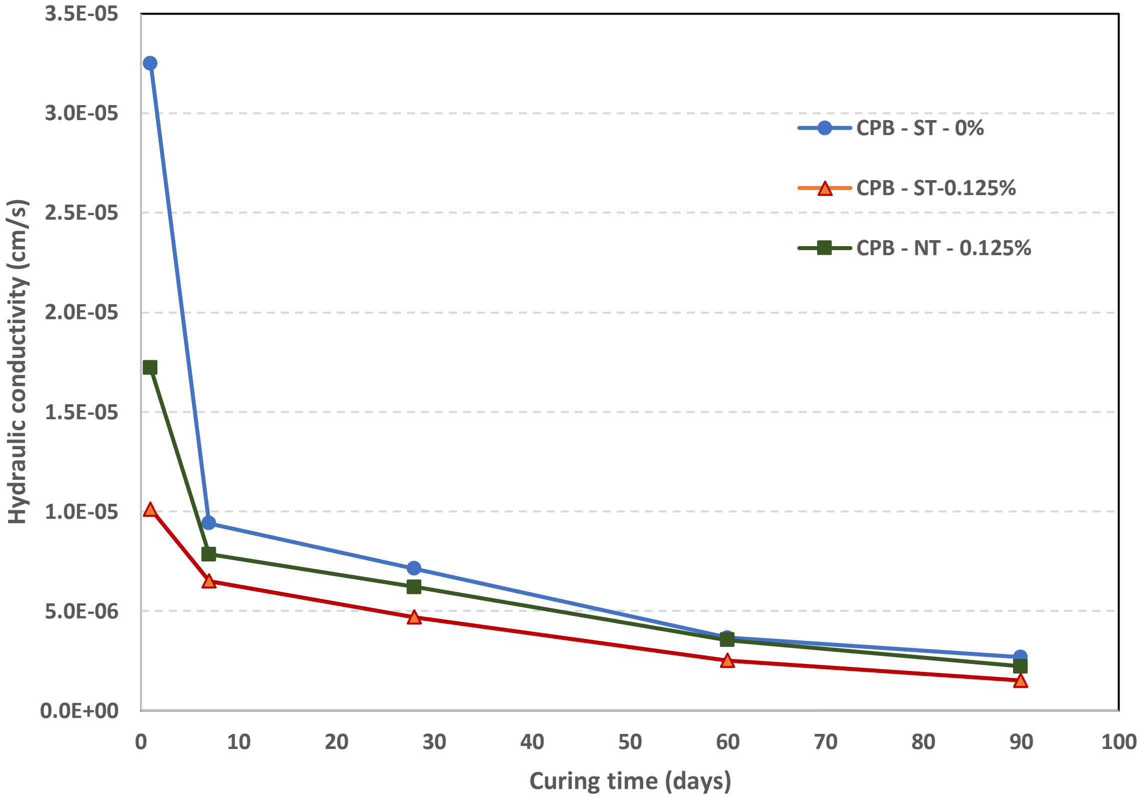
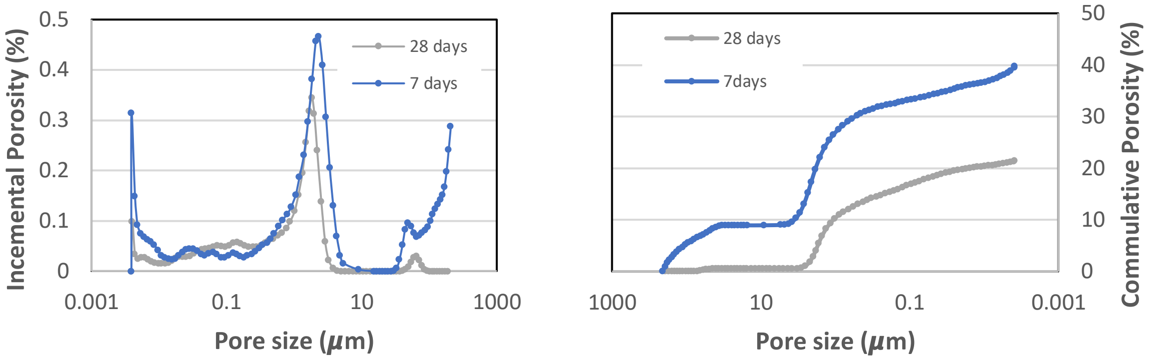


Figure 5.2. Evolution of hydraulic conductivity in CPB made with ST and NT



a) Pore size distribution b) Total pore volume

Figure 5.3. MIP graphs for CPB samples containing superplasticizer at different curing ages

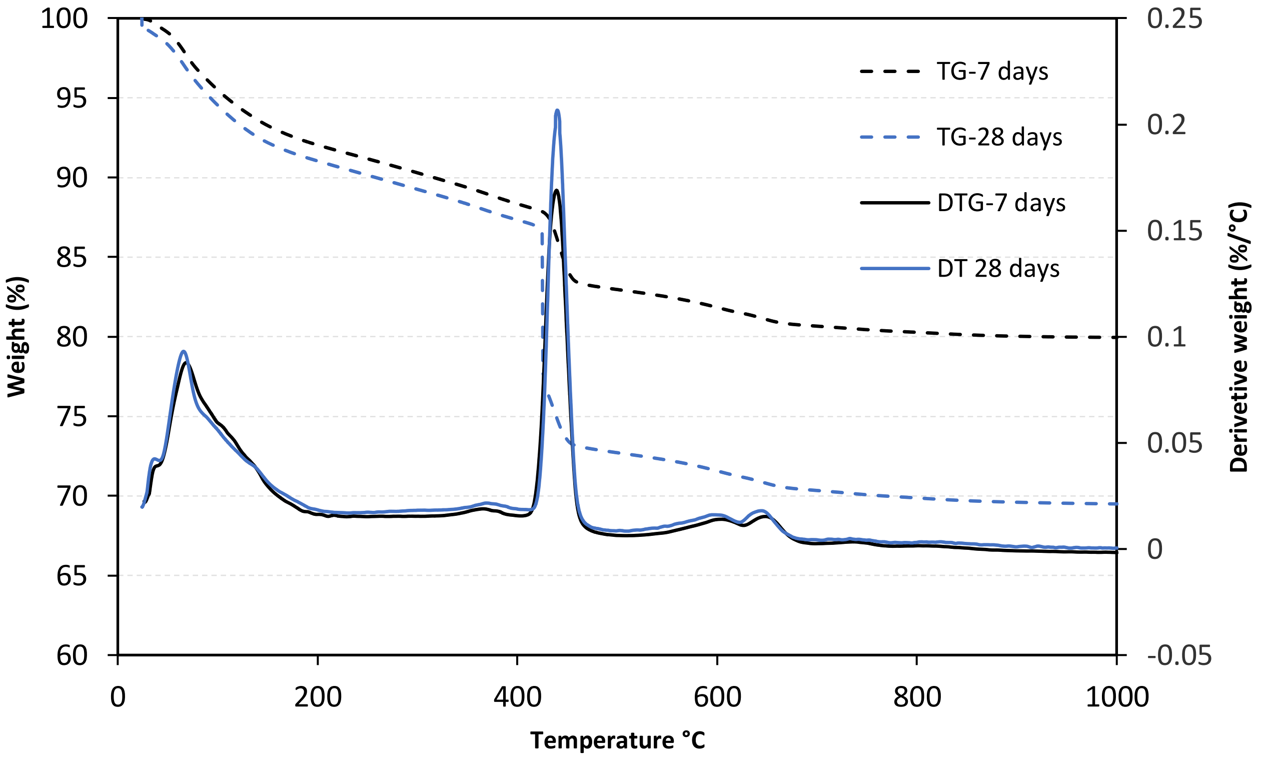


Figure 5.4. TG/DTG graphs of cement pastes containing superplasticizer cured for 7 and 28 days

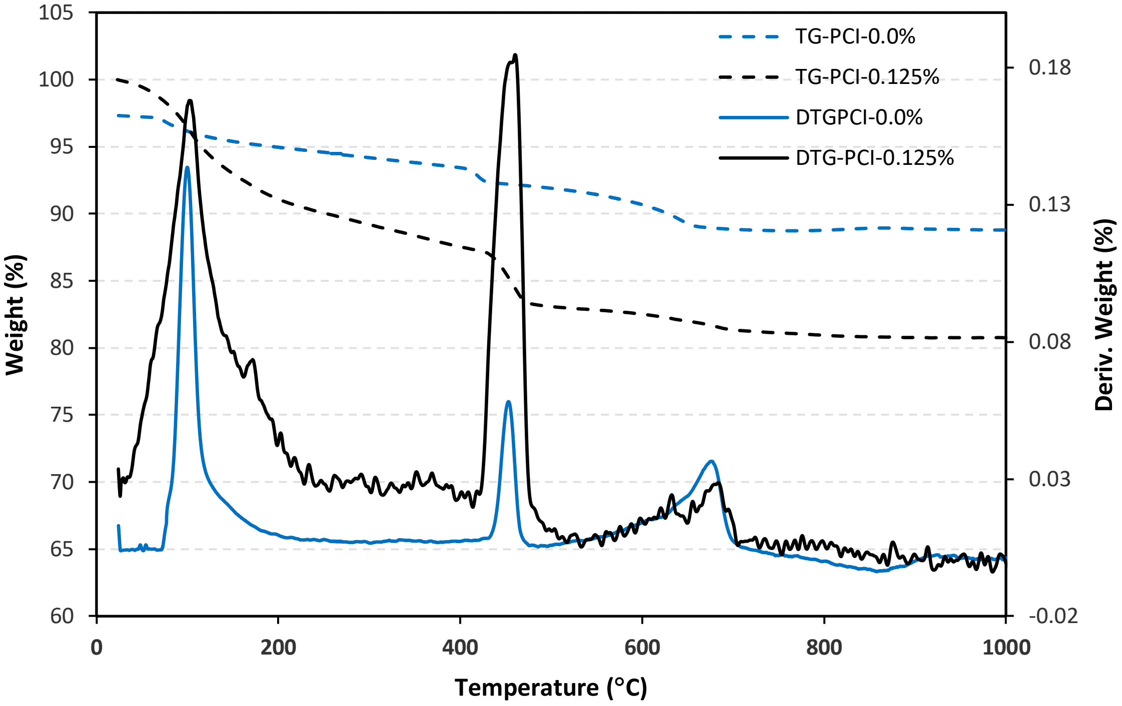
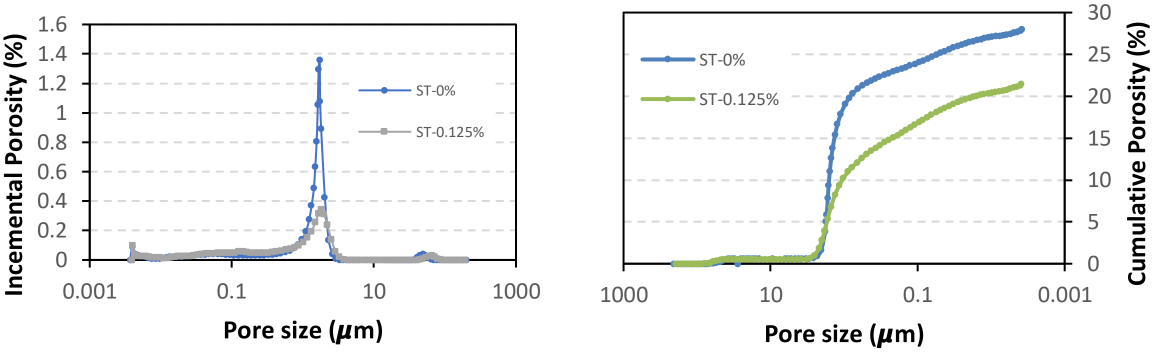


Figure 5.5. TG/DTG graphs of 7-day cement pastes with different superplasticizer contents



b) Pore size distribution b) Total pore volume

Figure 5.6. Effect of superplasticizer on the pore sizes and volume in the CPB cured for 28 days

5.3.2 Effect of temperature on the hydraulic conductivity

Curing temperature was also observed to influence the hydraulic conductivity of the CPB containing superplasticizer. Figure 5.7 presents the changes in the hydraulic conductivity of specimens prepared and cured at three different temperatures, 2 ^{o}C, 20 ^{o}C, and 35 ^{o}C. Throughout the curing period of 90 days, the CPB cured at 35 ^{o}C has the least hydraulic conductivity, followed by 20 ^{o}C, and then 2 ^{o}C. This is similar to what was observed from other studies on CPB and other cementitious materials (e.g. Fall et al., 2009; Wu & Cai, 2015; Palou et al., 2016; Liu B. et al.,2018), and thus, the presence of superplasticizer does not change the relationship. The MIP results (Figure 5.8) on CPB specimens with 0.125% superplasticizer cured at 20 ^{o}C and 35 ^{o}C temperatures are in agreement with the assertion. The quantity of large pores as well as the cumulative pore volume in the specimen with curing temperature of 2 ^{o}C is much higher than that in that with a curing temperature of 35 ^{o}C. A more suitable parameter that can give a better understanding on why the hydraulic conductivity is different based on the pore distribution is the threshold diameter. According to Aligizaki (2006), the threshold diameter, with respect to the mercury intrusion porosimetry, is the smallest pore size having geometric continuity throughout the sample thereby allowing uninhibited intrusion. This pore diameter is approximated to be the point of inflexion on the cumulative porosity curve (Aligizaki, 2006). From Figure 5.8 b, this diameter is approximately 3 µm for the 20 ^{o}C specimen and 0.08 µm for the 35oC specimen. This is an indication of finer pore structure in the 35 ^{o}C-CPB which translates to lower hydraulic conductivity.

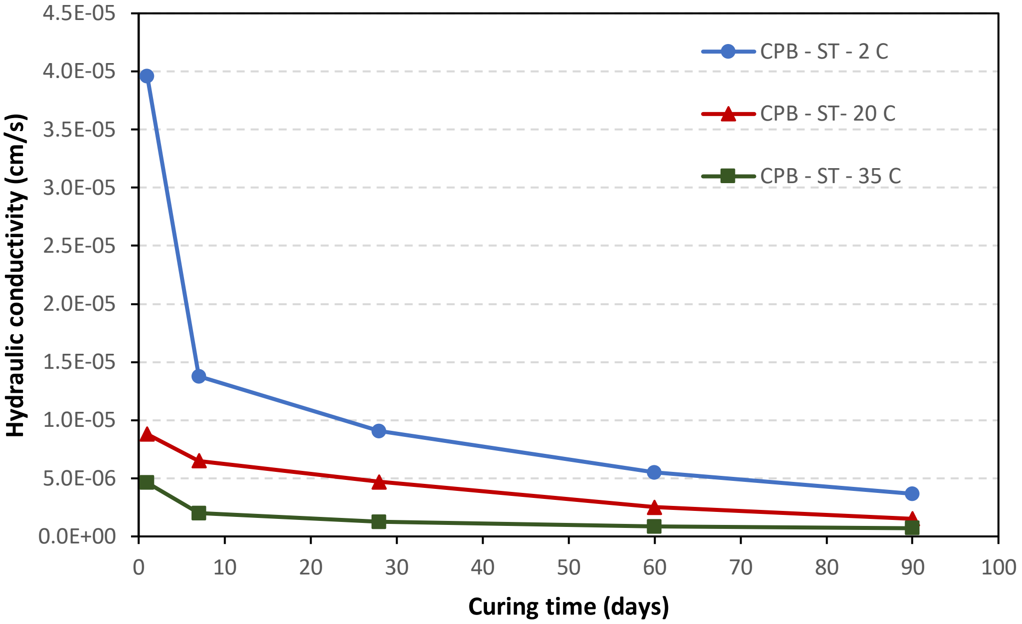
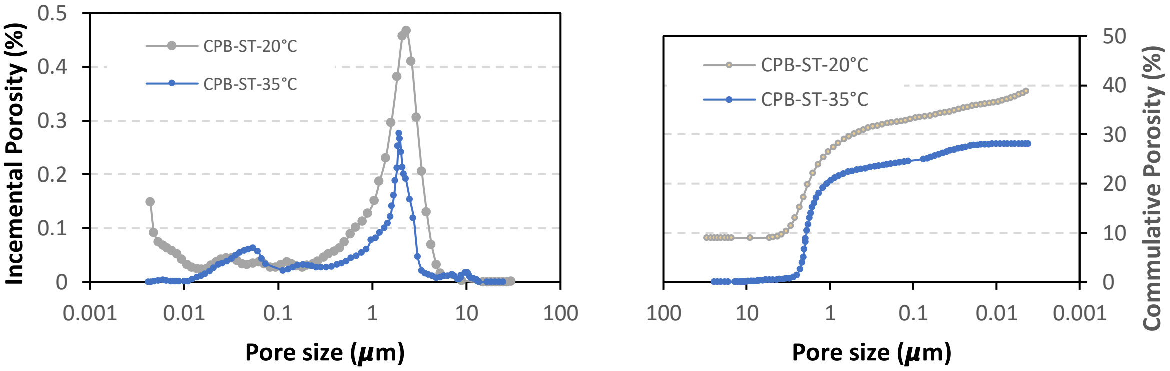


Figure 5.7. Temperature effect on the hydraulic conductivity of CPB containing 0.125% superplasticizer



a) Pore size distribution b) Total pore volume

Figure 5.8. MIP graphs for CPB samples containing superplasticizer with different curing temperatures

5.3.3 Effects of binder type on the hydraulic conductivity

Because the replacement of PCI with pozzolans is a common practice in the backfilling industry, the effects of FA and BFS in CPB containing superplasticizer were investigated in this study. The hydraulic conductivity plots of CPB made with three blending ratios (100% PCI; and 50/50 PCI/FA; 50/50 PCI/BFS) is shown in Figure 5.9. It can be noticed that the CPB containing PCI and FA has the highest hydraulic conductivity after 1 day and from 28 days onward. The sample containing PCI and BFS is the least permeable throughout the curing period. The reason for that can be attributed to the physical structure of the binders and the manner in which they react during the hydration process. Although BFS exhibits slow hydration reaction in the early age (Bouzoubaa and Foo 2004), its presence in the CPB could improve the hydraulic conductivity due to its filler effect. Slag has smaller particle size (with specific surface greater than PCI – Table 5.3) and is therefore capable of filling the spaces between cement and tailings particles (Kumar et al., 2008). Furthermore, the pozzolanic effect of the BFS begins once there is sufficient amount of CH from PCI hydration. The reaction between CH and the BFS produces additional CSH gel that contributes to less porosity in the material (Niu et al., 2002; Fall et al., 2009). However, FA does not act in the same way as the BGS on the overall hydration process. Its influence can be classified into dilution, physical and chemical effect (Narmluk & Nawa, 2011). Replacement of PCI with same quality of FA has been reported to increase the available water for hydration, which could subsequently improve the degree of cement hydration in concrete, a termed as dilution effect (Narmluk & Nawa, 2011; Zhang etal., 2012; Wang, 2014). However, FA may also slow down the hydration due to the physical nature of its particles. Even though it has greater specific surface area than PCI (Table 5.3), calcium ions adsorb on its surface and thus lowering the overall ions to participate in the chemical reaction (Langan et al., 2002; Rahhal & Talero, 2004). Similar to BFS, FA participates in the chemical reaction by reacting with the CH from the PCI hydration to generate C-S-H gel (Papadakis, 2000). Having the lowest percentage of CaO as shown in Table 5.3, this pozzolanic reaction will produce less hydration products as compared to BFS in the long term. The XRD graphs presented in Figure 5.10 are in agreement with the above assertions. The CPB containing the blend of PCI and BFS has the largest quantities of ettringite and C-S-Hm facilitating the filling of pores which is the reason for its low hydraulic conductivity. These results show that replacement of cement with BFS would improve the environmental performance of CPB containing superplasticizer with respect to fluid transport ability.

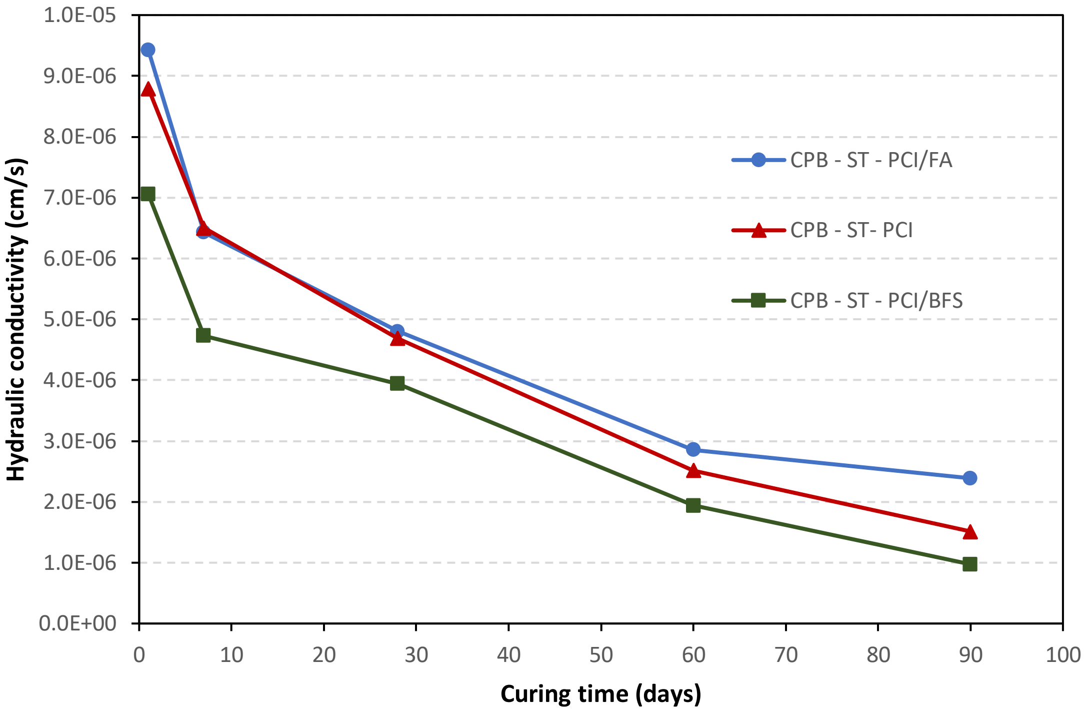
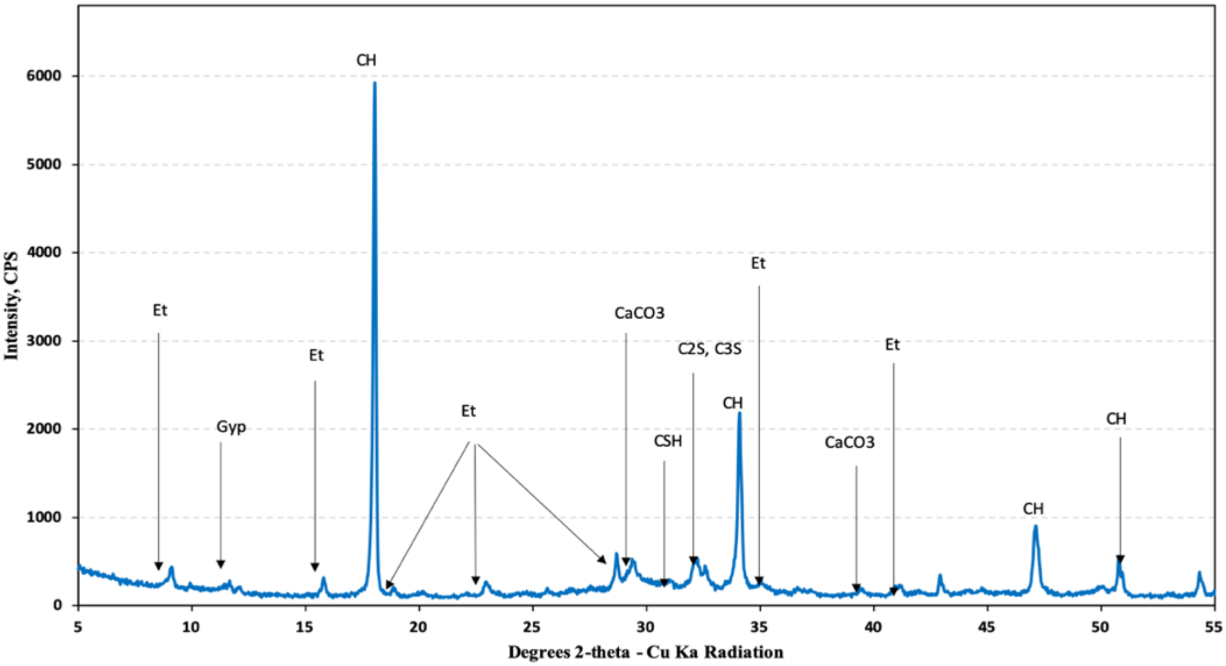
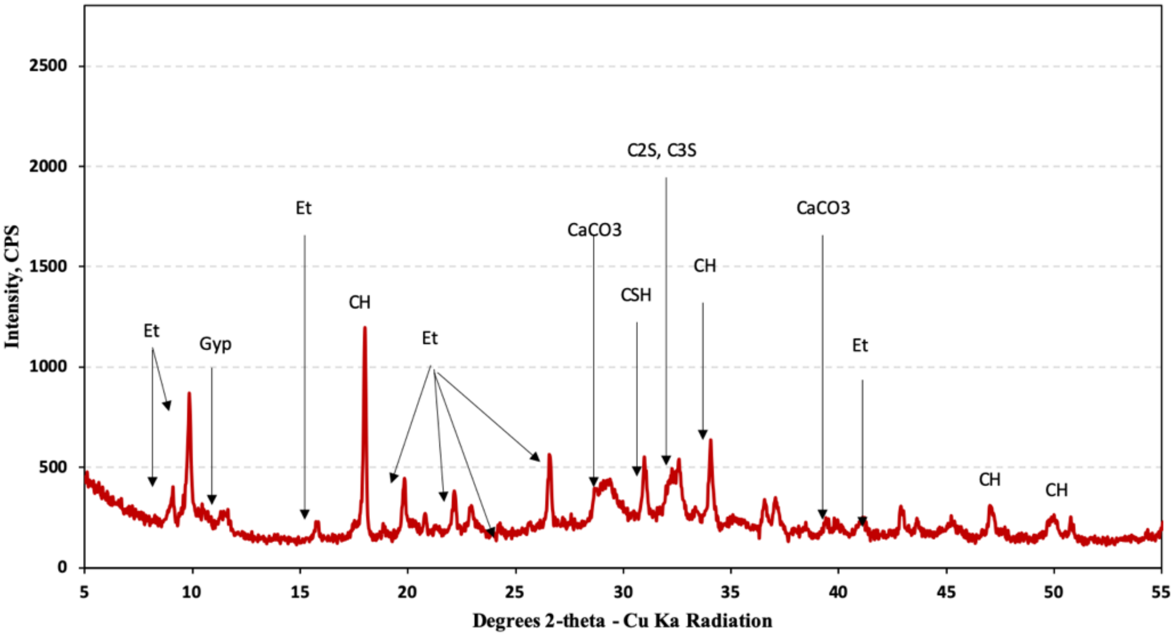


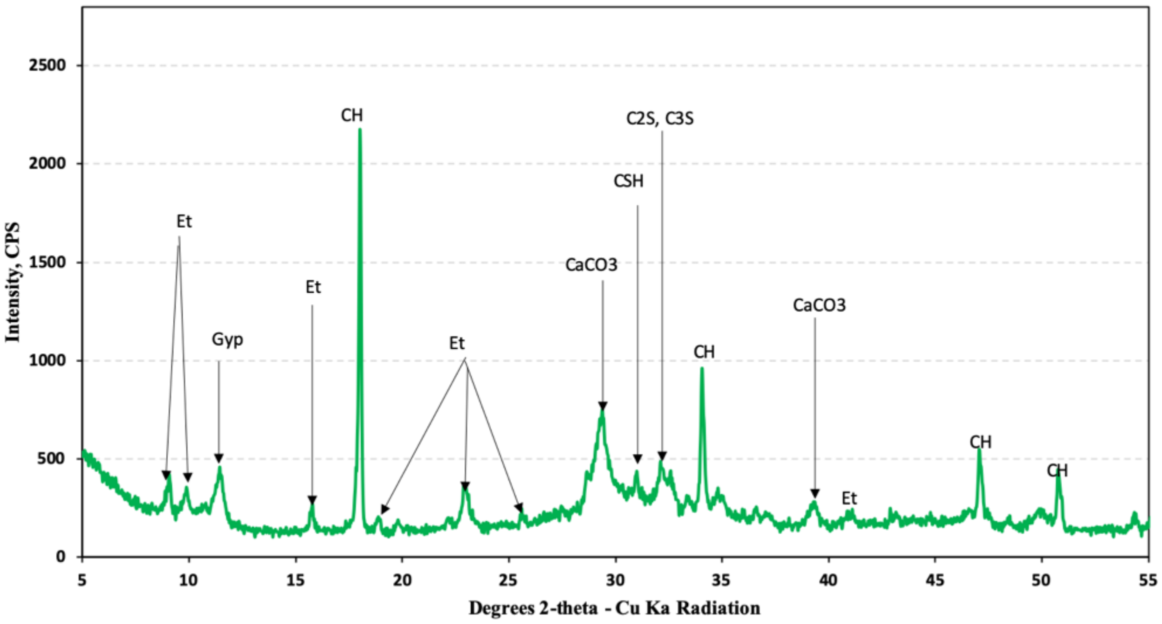
Figure 5.9. Effect of binder type on the hydraulic conductivity of CPB containing superplasticizer



a) CPB with 100% PCI



b) CPB with 50:50 blend of PCI and BFS



c) CPB with 50:50 blend of PCI and FA

Figure 5.10. XRD analysis results for 28 days specimens containing different binder proportions

5.3.4 Effect of W/C ratio on the hydraulic conductivity

Superplasticizers are added in cementitious construction materials to improve workability and/or flowability without the need to increase the water content beyond what is required for optimal performance. The changes in the hydraulic conductivity of CPB samples having different W/C ratios and constant amount of PCI and superplasticizer was investigated in this study. As shown in Figure 5.11, the W/C ratio has a positive correlation with the hydraulic conductivity. The is because of the negative effects of excess water on the porosity of CPB and other cementitious material (Kearsley & Wainwright, 2001; Fall et al. 2009, 2010; Shamsai et al., 2012). Indeed, increasing the W/C ratio produces large capillary pore content in the early age, i.e. in higher initial porosity and coarser pore structure in the material. Ultimately, this will result in slower filling of the CPB pores by the binder hydration products, thus leading to higher hydraulic conductivity values due to coarser pore structure and higher porosity. This is evident in the pore distributions of CPB specimens having W/C ratios of 5 and 7.35 shown in Figure 5.12. Thus, limiting the W/C ratio in CPB to a required proportion is beneficial towards the improvement of its permeability. These conclusions and explanations also agree with the MIP results discussed by Fall et al. (2009, 2010), showing that CPB with a higher W/C ratio has higher total porosity and coarser pore structure.

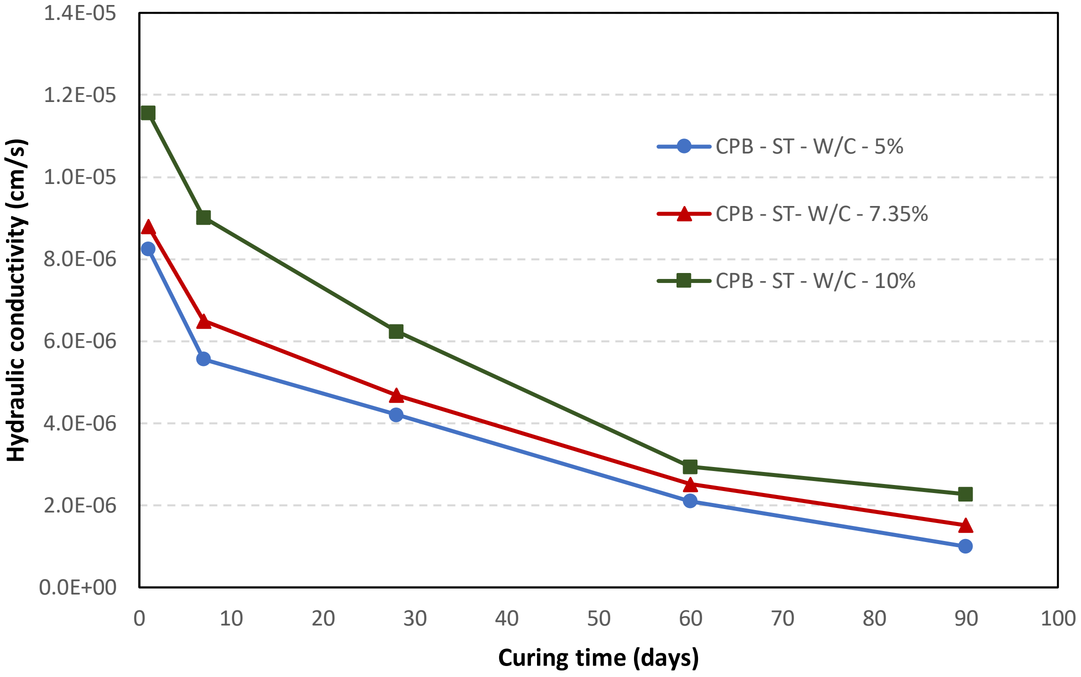
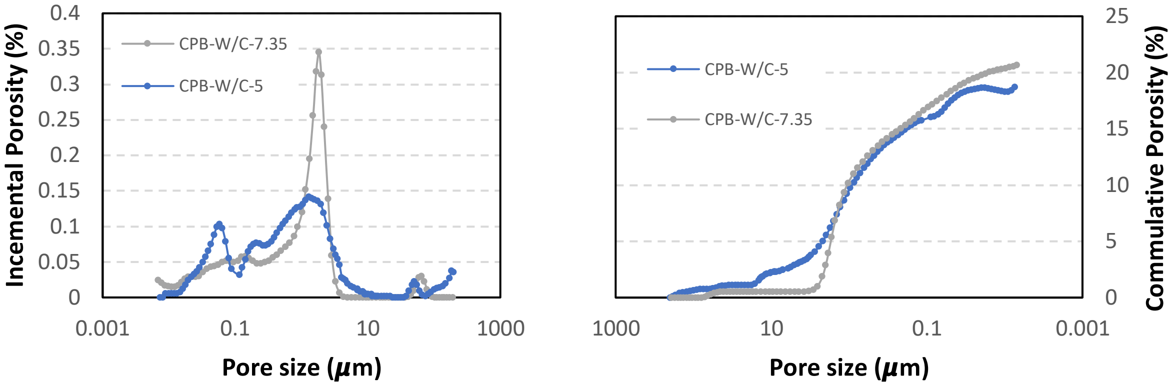


Figure 5.11. Effect of W/C ratio on the hydraulic conductivity of CPB containing superplasticizer



a) Pore size distribution b) Total pore volume

Figure 5.12. Effect of W/C ratio on the pore size and volume in the CPB samples containing superplasticizer

5.3.5 Effect of sulphate content on the hydraulic conductivity

Polycarboxylate-based superplasticizers are known to be sensitive to sulphate ions because both are adsorbed by the cement particles competitively (Pourchet et al., 2012; Pameijer, 2017). Therefore, it is important to study the combined effects of both chemical compounds on the CPB. Hydraulic conductivity of CPB specimens containing 0.125% superplasticizer with 0 ppm and 25,000 ppm sulphate contents is presented in Figure 5.13. The result indicates that the presence of sulphate in the CPB significantly reduces the hydraulic conductivity. This is likely due to the modification of the pore structure of the CPB by the reaction between the sulphate and the binder and cement hydration products (CH). Studies have shown that sulphate ions induce the precipitation of expansive minerals (i.e. ettringite, gypsum) owing to the reaction between the sulphate ions and the cement components (C_3A) and hydration products (e.g. Bellmann et al., 2006; Pokharel & Fall, 2013; Fall & Benzaazoua, 2005; Chen et al., 2019). These expansive minerals fill pores within the cemented matrix of the CPB material, and thus refining its pore structure and reducing its porosity. The pore distribution in the CPBs used in this study as seen from the MIP results in Figure 5.14 confirms that there is less porosity in the specimen containing sulphate. It is important to point out the little change in the hydraulic conductivity of the samples containing sulphate from 60 days to 90 days. There is a high tendency that the hydraulic conductivity of the 0 ppm sample would be less in the long term. This is expected because the excessive production of ettringite and gypsum due to sulphate eventually leads to cracks in the CPB (Li & Fall, 2016; Fang & Fall, 2019) and thus increasing the hydraulic conductivity.

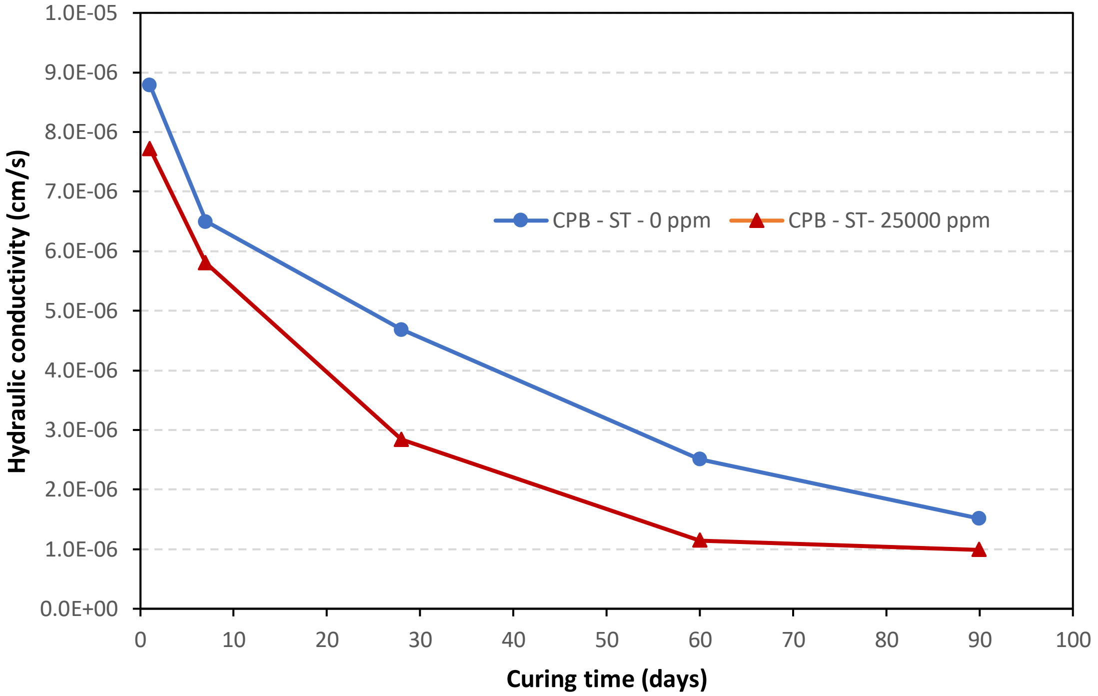
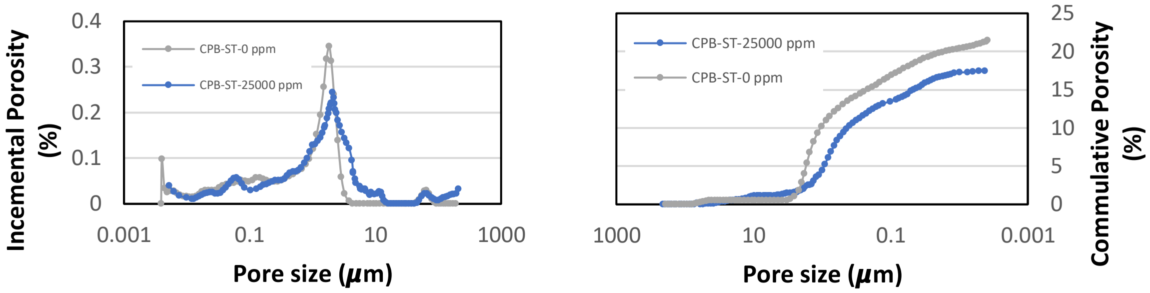


Figure 5.13. Effect of sulphate on the hydraulic conductivity of CPB containing superplasticizer



a) Pore size distribution b) Total pore volume

Figure 5.14. MIP graphs for CPB samples containing superplasticizer with different curing temperatures

5.4 Summary and conclusions

This experimental study highlighted the variations in the hydraulic conductivity of CPB containing polycarboxylate ether-based superplasticizer with different compositions and curing conditions. Vital conclusions drawn from the study findings are given below.

1. The addition of ether-based superplasticizer to the CPB decreases the hydraulic conductivity. The reduction is largely attributable to the influence of this superplasticizer on particles mobility and cement hydration.
2. The hydraulic conductivity decreases with curing time regardless of the mix composition, superplasticizer content, and curing condition. It generally decreases rapidly in the early age (0 to 7 days) and continues slowly beyond that.
3. Increase in the curing temperature results in a significant reduction of the hydraulic conductivity. This behavior is largely due to faster cement hydration at high temperatures which leads to more hydration products and finer pore structure.

4. Presence of sulphide minerals or sulphate ions in natural tailings influences the hydraulic conductivity by inducing an excessive generation of expansive compounds that fill the pores in the CPB.
5. Replacement of PCI with blast furnace slag significantly improves the hydraulic conductivity of CPB containing ether-based superplasticizer. However, replacement with fly ash has an opposite effect although the marginal changes are small.
6. High water to cement ratio produces CPB with high hydraulic conductivity implying that limiting the water to a required proportion is beneficial.

5.5 References

Aldhafeeri, A., Fall, M., Pokharel M., & Pouramini Z. (2016). Temperature dependency of the reactivity of cemented paste backfill. Applied Geochemistry 72:10-19.

Abdul-Hussain, N., & Fall, M. (2011). Unsaturated hydraulic properties of cemented tailings backfill that contains sodium silicate. *Engineering geology*, *123*(4), 288-301.

Akcil, A., & Koldas, S. (2006). Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of cleaner production*, *14*(12-13), 1139-1145.

Aligizaki, K.K. (2006). Pore structure of Cement-Based Materials: Testing, Interpretation and Requirements. *Taylor & Francis*, London

Alonso, C., & Fernandez, L. (2004). Dehydration and rehydration processes of cement paste exposed to high temperature environments. *Journal of materials science*, *39*(9), 3015-3024.

ASTM C143/C143M-15a. Standard test method for slump of hydraulic-cement concrete. West Conshohocken, PA: ASTM International; 2015. www.astm.org (accessed January 25, 2017).

Belem, T., Bussière, B., & Benzaazoua, M. (2001). The effect of microstructural evolution on the physical properties of paste backfill. In *Proc. of Tailings and Mine Waste* (Vol. 1, pp. 365-374).

Bellmann, F., Möser, B., & Stark, J. (2006). Influence of sulfate solution concentration on the formation of gypsum in sulfate resistance test specimen. *Cement and Concrete Research*, *36*(2), 358-363.

Bravo, M., de Brito, J., Evangelista, L., & Pacheco, J. (2017). Superplasticizer's efficiency on the mechanical properties of recycled aggregates concrete: Influence of recycled aggregates composition and incorporation ratio. *Construction and Building Materials*, *153*, 129-138.

Björnström, J., & Chandra, S. (2003). Effect of superplasticizers on the rheological properties of cements. *Materials and Structures*, *36*(10), 685-692.

Bouzoubaa, N., & Foo, S. (2004). Use of fly ash and slag in concrete: A Best Practice Guide. *Materials and Technology Laboratory, MTL*, *16*.

Bullard, J. W., Jennings, H. M., Livingston, R. A., Nonat, A., Scherer, G. W., Schweitzer, J. S., Karen S,.& Thomas, J. J. (2011). Mechanisms of cement hydration. *Cement and concrete research*, *41*(12), 1208-1223.

Chen, X., Shi, X., Zhou, J., Du, X., Chen, Q., & Qiu, X. (2019). Effect of overflow tailings properties on cemented paste backfill. *Journal of environmental management*, *235*, 133-144.

Cihangir, F., & Akyol, Y. (2018). Mechanical, hydrological and microstructural assessment of the durability of cemented paste backfill containing alkali-activated slag. *International Journal of Mining, Reclamation and Environment*, *32*(2), 123-143.

Cui, L., & Fall, M. (2016). An evolutive elasto-plastic model for cemented paste backfill. Computers & Geotechnics 71:19-29

Ercikdi B, Kesimal A, Cihangir F, Deveci H, Alp I (2009). Cemented paste backfill of sulphide-rich tailings: Importance of binder type and dosage. Cement and Concrete Composites 31(4):268-274

Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine tailings. *Water Resources Research*, *32*(6), 1773-1784.

Fall, M., Célestin, J.C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of temperature on the mechanical properties of cemented mine backfill. Engineering Geology 14 (3-4): 397-413.

Fall, M., & Pokharel, M. (2010). Coupled effects of sulphate and temperature on the strength development of cemented tailings backfills: Portland cement-paste backfill. Cement and Concrete Composites 32(10): 819-828.

Fall, M., Adrien, D., Célestin, J. C., Pokharel, M., & Touré, M. (2009a). Saturated hydraulic conductivity of cemented paste backfill. *Minerals Engineering*, *22*(15), 1307-1317.

Fall, M., Célestin, J.C., & Han, F.S. (2009b). Suitability of bentonite-paste tailings mixtures as engineering barrier material for mine waste containment facilities. Minerals Engineering 22 (9-10), 840-848

Fall, M., & Benzaazoua, M. (2005). Modeling the effect of sulphate on strength development of paste backfill and binder mixture optimization. *Cement and Concrete Research*, *35*(2), 301-314.

Fang, K., & Fall, M. (2019). Chemically Induced Changes in the Shear Behaviour of Interface Between Rock and Tailings Backfill Undergoing Cementation. *Rock Mechanics and Rock Engineering*, *52*(9), 3047-3062.

Fernandez-Alvarez, J. M., Duran, A., Navarro-Blasco, I. Í., Lanas, J., Sirera, R., & Alvarez, J. I. (2013). Influence of nanosilica and a polycarboxylate ether superplasticizer on the performance of lime mortars.

Fridjonsson, E. O., Hasan, A., Fourie, A. B., & Johns, M. L. (2013). Pore structure in a gold mine cemented paste backfill. *Minerals Engineering*, *53*, 144-151.

Gerasimov, A., Kotova, E., & Ustinov, I. (2019, September). Applied Mineralogy of

Anthropogenic Accessory Minerals. In *International Congress on Applied Mineralogy* (pp. 70-74). Springer, Cham.

Ghirian, A., & Fall, M. (2015). Coupled behavior of cemented paste backfill at early ages. *Geotechnical and Geological Engineering*, *33*(5), 1141-1166.

Gabrovšek, R., Vuk, T., & Kaučič, V. (2006). Evaluation of the hydration of Portland cement containing various carbonates by means of thermal analysis. *Acta Chim Slov*, *53*, 159-65.

Gelardi, G., & Flatt, R. J. (2016). Working mechanisms of water reducers and superplasticizers. In *Science and Technology of Concrete Admixtures* (pp. 257-278). Woodhead Publishing.

Godbout, J., Bussière, B., & Belem, T. (2007). Evolution of cemented paste backfill saturated hydraulic conductivity at early curing time.

Grabinsky, M., Bawden, W., Simon, D., & Thompson, B. (2008). In situ properties of cemented paste backfill in an Alimak stope. *Proceedings of GeoEdmonton*, *8*, 790-796.

Haruna, S., Fall, M. (2020). "Time-and temperature-dependent rheological properties of cemented paste backfill that contains superplasticizer." Powder Technology 360,731-740

He, Y., Zhang, X., Shui, L., Wang, Y., Gu, M., Wang, X., & Peng, L. (2019). Effects of PCEs with various carboxylic densities and functional groups on the fluidity and hydration performances of cement paste. *Construction and Building Materials*, *202*, 656-668.

Jacobs, J. A., & Testa, S. M. (2014). Acid Drainage and Sulfide Oxidation: Introduction. *Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, Prediction, Prevention, and Remediation*, 3.

Jennings, S. R., Blicker, P. S., & Neuman, D. R. (2008). *Acid mine drainage and effects on fish health and ecology: a review*. Reclamation Research Group.

Jiang H, Fall M, Cui L (2017). Freezing behaviour of cemented paste backfill material in column experiments. Construction and Building Materials 147, 837-846

Kauppi, A., Andersson, K. M., & Bergström, L. (2005). Probing the effect of superplasticizer adsorption on the surface forces using the colloidal probe AFM technique. *Cement and concrete research*, *35*(1), 133-140.

Ke, X., Zhou, X., Wang, X., Wang, T., Hou, H., & Zhou, M. (2016). Effect of tailings fineness on the pore structure development of cemented paste backfill. *Construction and Building Materials*, *126*, 345-350.

Kearsley, E. P., & Wainwright, P. J. (2001). Porosity and permeability of foamed concrete. *Cement and concrete research*, *31*(5), 805-812.

Kennedy, M. (2015). Petrophysical Properties. In *Developments in Petroleum Science* (Vol. 62, pp. 21-72). Elsevier.

Kumar, S., Kumar, R., Bandopadhyay, A., Alex, T. C., Kumar, B. R., Das, S. K., & Mehrotra, S. P. (2008). Mechanical activation of granulated blast furnace slag and its effect on the properties and structure of portland slag cement. *Cement and Concrete Composites*, *30*(8), 679-685.

Langan, B. W., Weng, K., & Ward, M. A. (2002). Effect of silica fume and fly ash on heat of hydration of Portland cement. *Cement and Concrete research*, *32*(7), 1045-1051.

Li, W., & Fall, M. (2018). Strength and self-desiccation of slag-cemented paste backfill at early ages: Link to initial sulphate concentration. Cement and Concrete Composites 89: 160-168.

Li, W., & Fall, M. (2016). Sulphate effect on the early age strength and self-desiccation of cemented paste backfill. *Construction and Building Materials*, *106*, 296-304.

Liu, B., Luo, G., & Xie, Y. (2018). Effect of curing conditions on the permeability of concrete with high volume mineral admixtures. *Construction and Building Materials*, *167*, 359-371.

Liu, R., Xiao, H., Li, H., Sun, L., Pi, Z., Waqar, G. Q., & Yu, L. (2018). Effects of nano-SiO 2 on the permeability-related properties of cement-based composites with different water/cement ratios. *Journal of materials science*, *53*(7), 4974-4986.

Lothenbach, B., Winnefeld, F., & Figi, R. (2007). The influence of superplasticizers on the hydration of Portland cement. *Empa, Dübendorf, Switzerland*.

Marchon, D., & Flatt, R. J. (2016). Mechanisms of cement hydration. In *Science and technology of concrete admixtures* (pp. 129-145). Woodhead Publishing.

Mollah, M. Y. A., Adams, W. J., Schennach, R., & Cocke, D. L. (2000). A review of cement superplasticizer interactions and their models. *Advances in Cement Research*, *12*(4), 153-161.

Narmluk, M., & Nawa, T. (2011). Effect of fly ash on the kinetics of Portland cement hydration at different curing temperatures. *Cement and Concrete Research*, *41*(6), 579-589.

Niu, Q., Feng, N., Yang, J., & Zheng, X. (2002). Effect of superfine slag powder on cement \ properties. *Cement and Concrete Research*, *32*(4), 615-621.

Orejarena, L., & Fall, M., (2011). Artificial neural network based modeling of the coupled effect of sulphate and temperature on the strength of cemented paste backfill. Canadian Journal of Civil Engineering 38 (1), 100-109

Ouellet, S., Bussiere, B., Aubertin, M., & Benzaazoua, M. (2008). Characterization of cemented paste backfill pore structure using SEM and IA analysis. *Bulletin of Engineering Geology and the Environment*, *67*(2), 139-152.

Palou, M. T., Kuzielová, E., Žemlička, M., Boháč, M., & Novotný, R. (2016). The effect of curing temperature on the hydration of binary Portland cement. *Journal of Thermal Analysis and Calorimetry*, *125*(3), 1301-1310.

Pameijer, C. H. (2017). Biocompatibility of luting cements for dental applications. In *Biocompatibility of Dental Biomaterials* (pp. 77-94). Woodhead Publishing.

Pane, I., & Hansen, W. (2005). Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cement and concrete research*, *35*(6), 1155-1164.

Papadakis, V. G. (2000). Effect of fly ash on Portland cement systems: Part II. High-calcium fly ash. *Cement and Concrete Research*, *30*(10), 1647-1654.

Piqué, T. M., Balzamo, H., & Vázquez, A. (2011). Evaluation of the hydration of portland cement modified with polyvinyl alcohol and nano clay. In *Key Engineering Materials* (Vol. 466, pp. 47-56). Trans Tech Publications Ltd.

Plank, J., & Hirsch, C. (2007). Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. *Cement and concrete research*, *37*(4), 537-542.

Pokharel, M., & Fall, M. (2013). Combined influence of sulphate and temperature on the saturated hydraulic conductivity of hardened cemented paste backfill. *Cement and Concrete Composites*, *38*, 21-28.

Pourchet, S., Liautaud, S., Rinaldi, D., & Pochard, I. (2012). Effect of the repartition of the PEG side chains on the adsorption and dispersion behaviors of PCP in presence of sulfate. *Cement and Concrete Research*, *42*(2), 431-439.

Puertas, F., Santos, H., Palacios, M., & Martínez-Ramírez, S. (2005). Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes. *Advances in Cement Research*, *17*(2), 77-89.

Rahhal, V., & Talero, R. (2004). Influence of two different fly ashes on the hydration of portland cements. *Journal of thermal analysis and calorimetry*, *78*(1), 191-205.

Ren, M., & Wang, X. (2019). Accessory Mineral Analysis of Alkali-rich Granite from Gejiu Tin District. *Microscopy and Microanalysis*, *25*(S2), 2322-2323.

Roshani, A., Fall, M., & Kennedy, K, (2017). Impact of drying on geo-environmental properties of mature fine tailings pre-dewatered with super absorbent polymer. International journal of environmental science and technology 14 (3), 453-462

Shamsai, A., Peroti, S., Rahmani, K., & Rahemi, L. (2012). Effect of water-cement ratio on abrasive strength, porosity and permeability of nano-silica concrete. *World Applied Sciences Journal*, *17*(8), 929-933.

Silvester, E. J., Bruckard, W. J., & Woodcock, J. T. (2011). Surface and chemical properties of chlorite in relation to its flotation and depression. *Mineral Processing and Extractive Metallurgy*, *120*(2), 65-70.

Simate, G. S., & Ndlovu, S. (2014). Acid mine drainage: Challenges and opportunities. *Journal of Environmental Chemical Engineering*, *2*(3), 1785-1803.

Tariq, A., & Nehdi, M. (2007, November). Developing durable paste backfill from sulphidic tailings. In *Proceedings of the Institution of Civil Engineers-Waste and Resource Management* (Vol. 160, No. 4, pp. 155-166). Thomas Telford Ltd.

Vaughan, D. J., & Lennie, A. R. (1991). The iron sulphide minerals: their chemistry and role in nature. *Science Progress (1933-)*, 371-388.

Veenstra, R. L., Grabinsky, M. W., Bawden, W. F., & Thompson, B. D. (2014, May). A numerical analysis of how permeability affects the development of pore water pressure in early age cemented paste backfill in a backfilled stope. In *Proceedings of the Eleventh*

International Symposium on Mining with Backfill (pp. 83-95). Australian Centre for Geomechanics.

Vakhshouri, B., & Nejadi, S. (2017). Compressive strength and mixture proportions of self-compacting lightweight concrete. *Comput. Concr*, *19*, 555-566.

Wang, Y., Fall, M., & Wu, A. (2016). Initial temperature-dependence of strength development and self-desiccation in cemented paste backfill that contains sodium silicate. Cement and Concrete Composites 67:101-110

Wang, X. Y. (2014). Effect of fly ash on properties evolution of cement based materials. *Construction and Building Materials*, *69*, 32-40.

Wu, D., & Cai, S. J. (2015). Coupled effect of cement hydration and temperature on hydraulic behavior of cemented tailings backfill. *Journal of Central South University*, *22*(5), 1956-1964.

Wu, D., Fall, M., & Cai, S. J. (2014). Numerical modelling of thermally and hydraulically coupled processes in hydrating cemented tailings backfill columns. *International Journal of Mining, Reclamation and Environment, 28*(3), 173-199.

Wu, Q., An, X., & Liu, C. (2014). Effect of polycarboxylate-type superplasticizer on the paste fluidity based on the water film thickness of flocs. *Science China Technological Sciences*, *57*(8), 1522-1531.

Yilmaz, E., Belem, T., Bussière, B., Mbonimpa, M., & Benzaazoua, M. (2015). Curing time effect on consolidation behaviour of cemented paste backfill containing different cement types and contents. *Construction and Building Materials*, *75*, 99-111.

Zhang, Y. R., Kong, X. M., Lu, Z. B., Lu, Z. C., & Hou, S. S. (2015). Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes. *Cement and Concrete Research*, *67,* 184-196.

Zhang, Q., Liu, J., Liu, J., Han, F., & Lin, W. (2016). Effect of superplasticizers on apparent viscosity of

cement-based material with a low water–binder ratio. *Journal of Materials in Civil Engineering*, *28*(9), 04016085.

Zeng, Q., Li, K., Fen-chong, T., & Dangla, P. (2012). Determination of cement hydration and pozzolanic reaction extents for fly-ash cement pastes. *Construction and Building Materials*, *27*(1), 560-569.

Zhou, Q., & Glasser, F. P. (2001). Thermal stability and decomposition mechanisms of ettringite at< 120 C. *Cement and Concrete Research*, *31*(9), 1333-1339.

Chapter 6. Technical Paper IV: Reactivity of cemented paste backfill containing polycarboxylate-based superplasticizer

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Abstract

Superplasticizers are used in the preparation of cemented paste backfill (CPB) to improve its rheological properties. Unlike other cementitious materials, the effects of superplasticizers on the performance of CPB have not been extensively studied. For example, CPB made with sulphide bearing tailings can generate acid mine drainage (AMD) which influences its environmental performance. AMD can be measured by the reactivity of the CPB when exposed to the atmosphere. This paper presents findings from experimental investigations on the effects of polycarboxylate superplasticizers (PCSP) on the reactivity of CPB containing pyrite. The reactivity of cured CPB specimens was determined by monitoring the rate of oxygen consumption in an enclosed chamber. Microstructural tests, namely mercury intrusion porosimetry, X-ray diffraction, and thermogravimetric analyses were also carried out to have a better understanding of the reactive mechanisms. The results obtained show that the addition of PCSP leads to a proportionate reduction of the reactivity. The admixture causes the refinement of the pore structure of the CPB by mainly improving the binder hydration and self-consolidation. It was also observed that less pyrite crystals were present in the CPB containing the superplasticizer. High curing temperature was also found to improve the binder hydration, leading to a decrease in reactivity. Partial replacement of cement with fly ash and blast furnace slag also decreases the reactivity due to the micro-filer effects on the CPB pore structure. These research findings will be valuable for the design of cost-effective and sustainable CPB structures.

Keywords: cemented paste backfill, reactivity, oxygen consumption test, acid mine drainage, tailings management, superplasticizer.

6.1 Introduction

A safe and sustainable disposable of tailings (the by-product of the milling of mineral ores) has been a challenge to the mining industry for a long time. It constitutes the bulk mass of the mining raw material, which, for some mines, can reach up to 99 per cent of the overall processed ore (Lottermoser, 2010). A tailings disposal approach that is proving to be effective and sustainable is their reuse as the principal constituent for a backfilling material called cemented paste backfill (CPB). Dewatered tailings (70-85 wt.% solids) are mixed with a hydraulic binder, water, and certain admixtures, when needed, to produce the CPB (Fall et al., 2008). The CPB technology is advantageous towards improvement of the mining productivity largely through reinforcement of ore pillars. Providing such support minimizes the risk of ground subsidence, ensures the safety or the workers, and increases ore recovery rate (Belem and Benzaazoua, 2008; Li, 2021).

Depending on the mineralogy of the ore, the tailings may contain a range of chemical elements and compounds that could be toxic to the environment or have the tendency of producing other harmful compounds upon undergoing chemical transformation (de Andrade et al., 2008; Kossoff et al., 2014). The generation of such chemical compounds may be more noticeable within tailings disposed on the ground surface (Edraki et al., 2014; Mohapatra and Kirpalani, 2017), but could also be observed in the tailings material used for backfilling (Benzaazoua et al., 2004). A common mechanism of how such toxic chemicals can be produced is the acid mine drainage (AMD), which refers to the process whereby acidic water is generated from sulfide-rich materials in the presence of water and oxygen (Akcil and Koldas, 2006; Dold, 2014). A typical sulphide mineral that is commonly found in most tailings is pyrite (FeS_2). A step-by-step oxidation process of pyrite as described by Jennings et al. (2008) is presented by the equations 1 through 4. Other sulfide minerals, such as bornite, chalcopyrite, arsenopyrite, and galena, undergo similar chemical reactions under similar conditions (Dold, 2014).

$$2\mathrm{FeS}_{2(\mathrm{s})} + 7\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{Fe}^{2+} + 4\mathrm{SO}^{2-}_{4(\mathrm{aq})} + 4\mathrm{H}^{+}_{(\mathrm{aq})} \qquad \textit{equation}\ \ 6.1$$

$$4\mathrm{Fe}^{2+}_{(\mathrm{aq})} + \mathrm{O}_2 + 4\mathrm{H}^{+}_{(\mathrm{aq})} \rightarrow 4\mathrm{Fe}^{3+}_{(\mathrm{aq})} + 2\mathrm{H}_2\mathrm{O} \qquad \mathrm{eqution}\ \ 6.2$$

$$2Fe^{3+} + 6\mathrm{H}_2\mathrm{O} \rightleftharpoons 2\mathrm{Fe(OH)}_{3(\mathrm{s})} + 6\mathrm{H}^{+}_{(\mathrm{aq})} \qquad \textit{equation}\ \ 6.3$$

$$14Fe^{3+} + \mathrm{FeS}_{2(\mathrm{s})} + 8\mathrm{H}_2\mathrm{O} \rightarrow 15\mathrm{Fe}^{2+}_{(\mathrm{aq})} + 2\mathrm{SO}^{2-}_{4} + 16\mathrm{H}^{+}_{(\mathrm{aq})} \qquad \textit{equation}\ \ 6.4$$

Chemical admixtures often added to the CPB to enhance certain properties have a tendency of influencing chemical reactions in cementitious materials (Prezzi, et al., 1998; Poole et al., 2011; Marchon and Flatt, 2016). One of such admixtures is the superplasticizer, which is used in the CPB for the improvement of rheological properties. Superplasticizers are high-range water-reducing admixtures that can reduce the water content of cementitious materials by 12-30% while maintaining a desirable flowability (Barabanshchikov and Komarinskiy, 2014). A study by Griesser (2002) showed that the efficacy of superplasticizers is influenced by their chemical interaction with the composition of cement clinker, the presence of sulphate ions in the pore water, and the nature of the superplasticizer molecules. Such interaction has been shown to influence both fresh and hardened properties of cementitious materials such as rheology, setting times, and compressive strength (Liao et al., 2006; Pei et al., 2008). Despite such documented effects of superplasticizers on cement hydration and other properties, no study has been conducted to investigate their influence on the reactivity of tailings (i.e., sulfides oxidation) in CPB.

One of the common superplasticizer types used in CPB is the polycarboxylate polymer-based surfactant (polycarboxylate-based superplasticizer or PCSP). It is an organic compound made up of molecules of carboxyl grafted copolymer with comb-shaped structures (Ilg and Plank, 2019). PCSPs achieve a high water reduction rate through two main mechanisms: electrostatic repulsion and steric hindrance (Pereira et al., 2012). Electrostatic repulsion, which is the major force through which most superplasticizers work, keeps colloidal particles apart due to the charge of the electrical double layer surrounding them (Tadros, 2013; Gelardi and Flatt, 2016). On the other hand, steric hindrance is an anti-flocculation effect induced by the comb-shaped molecules of the PCSPs which encapsulate the cement particles in the cementitious material (Bravo et al., 2017). It is the main mechanism that governs the activity of PCSPs (Gui et al., 2011; Bravo et al., 2017). Zingg et al. (2009) investigated the interactions of three types of the PCS with cement containing varying contents of C_3A. They found out that the amount of C_3A in a mixture significantly affects the rheological change inducted by the superplasticizer. A review by Sha et al. (2019) highlighted variations in the adsorption capacity of the same types of superplasticizers based on their dominant polymer-chain group and the amount of sulfate ions in a mixture. Evidently, the behaviour of the PCSP varies based on the chemical environment in a mixture and has a tendency of influencing the chemical reactions in a cementitious material such as CPB.

Based on overwhelming evidence on the effects of superplasticizers on the chemical reactions in cementitious materials, it is pertinent to know how they would affect the AMD generation in CPB containing sulphidic compounds. Therefore, this study was at investigating the reactivity of CPB containing PCSP using an oxygen consumption test, which allows for the monitoring of the oxidation rate of the pyrite in the CPB. The effects of superplasticizer content, curing temperature, binder type, and content were studied.

6. 2 Materials and methods

6.2.1. Materials

6.2.1.1 Tailings

The main constituent materials in the preparation of the CPB used in the study are the tailings. Two types, synthetic silica tailings (ST) and natural gold tailings (GT) were used. The ST are basically pure ground silica (manufactured by the U.S. Silica Co.) made-up of 99.8% quartz (SiO_2). It is used in experimental studies for its similarity with common mine tailings in terms of physical characteristics and lack of reactive chemical compounds that may create result uncertainties. The grain size distributions of the tailings together with the average of nine Canadian mines are shown in Figure 6.1. The GT was collected from a gold mine in Canada. With the percentage of materials finer than 20 µm ranging from 36 to 50 wt%, all the tailings could be classified as medium tailings (medium tailings vary from 35 to 60 wt%, according to Landriault, 2001). The physical properties and mineralogical compositions of the two types of tailings are presented in Tables 6.1 and 6.2.

Table 6.1. Physical properties of the tailings

Material	Physical properties						
	G_s	D_{10} (µm)	D_{30} (µm)	D_{50} (µm)	D_{60} (µm)	C_u	C_c
ST	2.7	1.9	9.0	22.5	31.5	16.6	1.4
NT	3.1	3.2	15.8	35.5	49.5	15.5	1.6

G_s = specific gravity; C_u = coefficient of uniformity; C_c = coefficient of curvature; D_x = diameter corresponding to x % of material passing the mechanical sieves,

Table 6.2. Mineralogical composition of the tailings

Tailings	Mineral											
	Quartz	Albite	Dolomite	Calcite	Chlorite	Magnetite	Pyrite	Talc	Pyrrhotite	Spinel	Others	Total
ST (w_t%)	99.8	-	-	-	-	-	-	-	-	-	0.2	100
NT (w_t%)	15	32.8	15	4.2	16.1	2.4	1	7	1.8	1.8	2.9	100

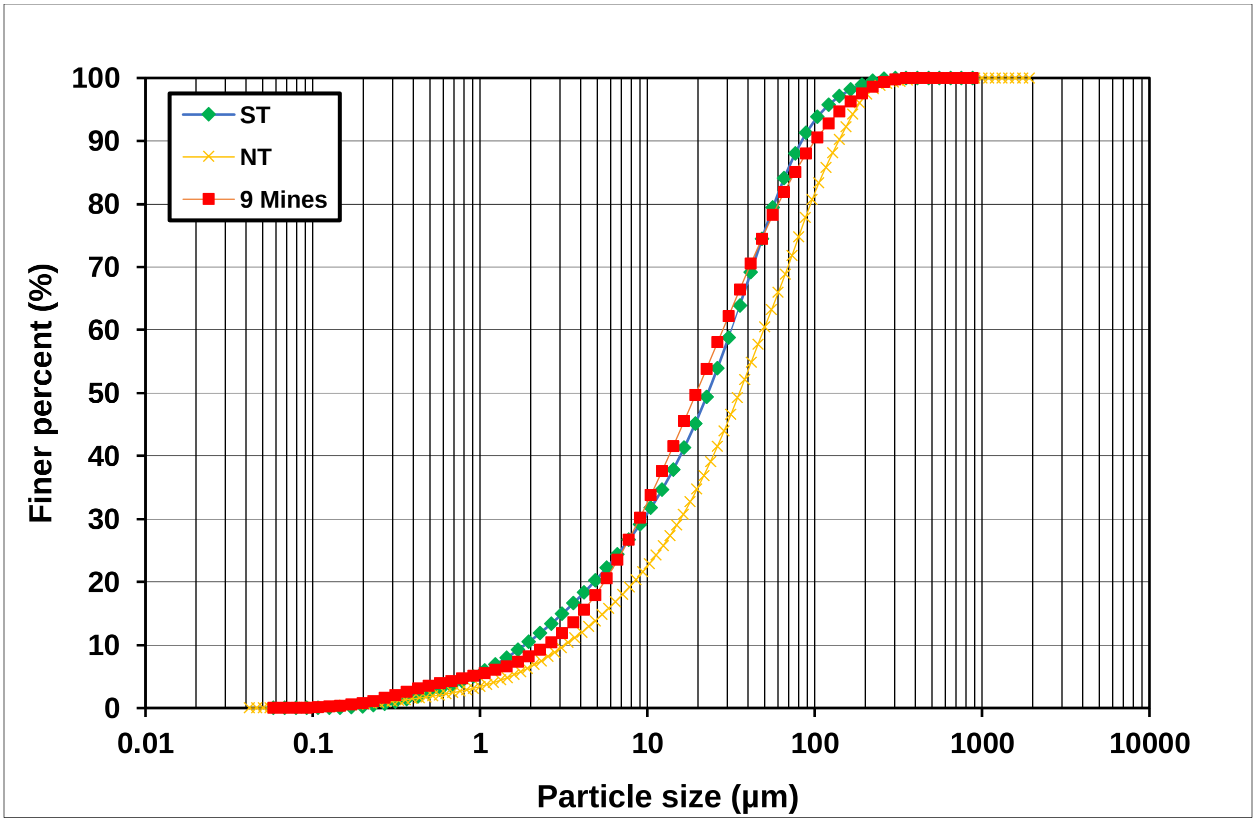


Figure 6.1. Grain size distribution of the tailings and coarse-grained sand used in this research with the average of 9 Canadian mine tailings

6.2.1.2 Binder and water

The binder is an important component of the CPB that is added to improve the mechanical properties. In this study, Portland cement type I (PCI) with the oxides composition presented in Table 6.3 was used as the primary binder. Portable tap water was used as the mixing water.

Table 6.3. Physical and chemical properties of the PCI

Binder Type	**MgO (wt.%)**	**CaO (wt.%)**	**SiO_2 (wt.%)**	**Al_2O_3 (wt.%)**	**Fe_2O_3 (wt.%)**	**SO_3 (wt.%)**	**Relative Density**	**Specific surface area (cm^2/g)**
PCI	2.65	62.82	18.03	4.53	2.70	3.82	3.1	1300
FA	5.58	21.47	38.06	19.45	5.33	2.7	2.6	2200
Slag	10.98	41.14	34.32	9.54	-	3.87	2.8	2100

6.2.1.2 Superplasticizer

A superplasticizer with the commercial name of Master Glenium 7500 (product of Badische Anilino und Soda Fabrik, Germany) was used in the study. It is a polycarboxylate ether-based, high range water-reducing admixture that is capable of reducing the mixing water requirement by up to 40%. It satisfies the requirements of the ASTM standard C494M for full-range water-reducing admixtures (ASTM, 2015).

6.2.1.3 Pyrite

To study the reactivity of the CPB materials, different percentages of pyrite powder (manufactured by Washington Mills North Grafton, Incl.) was added to the mixture. The properties of pyrite (Table 6.4) were similar to that of the common pyrite minerals found in natural tailings.

Table 6.4. Physical properties of the pyrite

Bulk density (g/cm^3)	**Density at 20 ºC (g/cm^3)**	**G$_s$**	**pH**	**Melting point (ºC)**
2.35	3.1	3.2	15.8	35.5

6.2.2. Sample preparation and curing

CPB samples with different proportions of tailings, binder, pyrite, and PCSP were prepared and cured at different curing temperatures as shown in Table 5. For each sample group, weighed solid content (tailings, binder and pyrite) were first mixed in a mechanical mixer for 2 minutes. The mixing water containing the appropriate portion of PCSP was added, and the mechanical mixer was run for another 5 minutes to achieve a homogenous CPB mix. The fresh CPB was cast into an air-tight plastic mould of 5 cm in diameter and 10 cm in height. The samples were cured by keeping them in temperature-controlled chambers until the time of testing.

6.2.2. Oxygen consumption test

The reactivity of the CPB samples was determined using the oxygen consumption (OC) as proposed by Elberling and Nicholson (1996). The approach is based on a steady rate of the change in oxygen concentration during an oxidation reaction. After curing the sample for the respective duration, a 2 cm deep chamber was created in the 5 cm diameter mould by digging off part of the CPB at the top. The mould was covered with a cap equipped with a GC33-200 oxygen sensor (GC Industries, USA) as shown in Figure 6.2. The sensor, which has an accuracy of up to 0.001 O_2, measures the voltage across the conductive air chamber, which can be fitted linearly with the concentration of oxygen (Elberling et al., 2000). As the exposed CPB material reacts, the oxygen concentration will continue to decrease based on the reaction rate of the sulphidic compounds. Voltage readings and logging were achieved using a Hantek 365 A USB multimeter connected to a computer. Each test was performed at least three times to ensure the reproducibility of results. The flux of oxygen per unit area of the specimen is calculated using equation 6.5.

$$F_S = C_0(kD_e)^{0.5} \qquad \textit{equation 6.5}$$

Where C_0 is the initial concentration of oxygen, which corresponds to the amount of oxygen in the atmosphere (20.95%); and the parameter *kDe* corresponds to the slope of the linear graph of C/C_0 versus time. The graph is plotted based on Fick's law given by equation 6.6.

$$\mathrm{Ln}\left(\frac{C}{C_0}\right) = -t\,(kD_e)^{0.5}\left(\frac{A}{V}\right) \qquad \textit{equation 6.6}$$

A is the surface area of the specimen exposed in the air chamber, and *V* is the volume of the chamber.

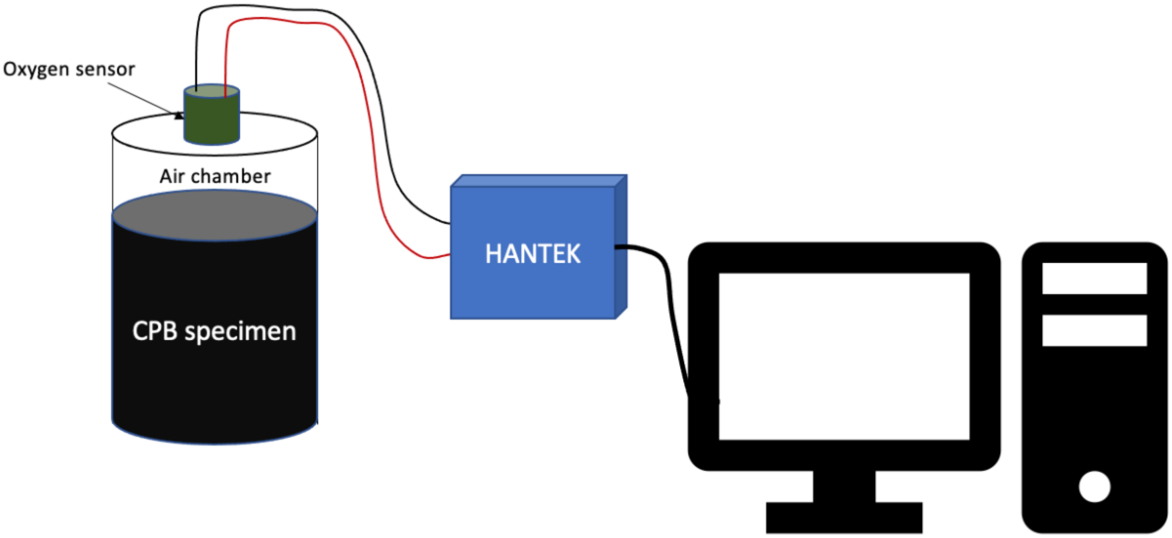


Figure 6.2. Setup for the oxygen consumption test

Figure 6. 3. Mix compositions for CPB specimens

Sample Name	**Binder content (%)**	**% PCI in the binder**	**% FA in the binder**	**%Slag in the binder**	**Tailings Type**	**W/C ratio**	**Superplasticizer content (%)**	**Pyrite content (%)**	**Curing Temperature (ºC)**	**Curing Period (days)**
A. Effect of curing time and superplasticizer on the reactivity of CPB										
CPB – 0%	4.5	100	0	0	ST	7.35	0.0	15	20	7, 28, 60, 90
CPB – 0.05%	4.5	100	0	0	ST	7.35	0.05	15	20	7, 28, 60, 90
CPB – 0.125%	4.5	100	0	0	ST	7.35	0.125	15	20	7, 28, 60, 90
CPB – 0.25%	4.5	100	0	0	ST	7.35	0.25	15	20	7, 28, 60, 90
B. Effect of curing time and superplasticizer on the reactivity of CPB										
CPB – NT– 0%	4.5	100	0	0	ST	7.35	0.0	15	20	7, 28, 60, 90
CPB – NT – 0.05%	4.5	100	0	0	ST	7.35	0.05	15	20	7, 28, 60, 90
CPB – NT – 0.125%	4.5	100	0	0	ST	7.35	0.125	15	20	7, 28, 60, 90
CPB – NT – 0.25%	4.5	100	0	0	ST	7.35	0.25	15	20	7, 28, 60, 90
C. Effect of temperature on the reactivity of CPB containing superplasticizer										
CPB – 0.125 – Tem 2	4.5	100	0	0	ST	7.35	0.125	15	2	7, 28, 60, 90

CPB – 0.125 – Tem 20	4.5	100	0	0	ST	7.35	0.125	15	20	7, 28, 60, 90
CPB – 0.125 – Tem 35	4.5	100	0	0	ST	7.35	0.125	15	35	7, 28, 60, 90
D. Effect of pyrite content on the reactivity of CPB containing superplasticizer										
CPB – 0.125 – 5% pyrite	4.5	100	0	0	ST	7.35	0.125	5	20	7, 28, 60, 90
CPB – 0.125 – 5% pyrite	4.5	100	0	0	ST	7.35	0.125	15	20	7, 28, 60, 90
CPB – 0.125 – 5% pyrite	4.5	100	0	0	ST	7.35	0.125	45	20	7, 28, 60, 90
E. Effect of binder type on the reactivity of CPB containing superplasticizer										
CPB – 0.125-PCI	4.5	100	0	0	ST	7.35	0.125	15	20	7, 28, 60, 90
CPB – 0.125-PCI/FA	4.5	50	50	0	ST	7.35	0.125	15	20	7, 28, 60, 90
CPB – 0.125-PCI/Slag	4.5	50	0	50	ST	7.35	0.125	15	20	7, 28, 60, 90
F. Effect of binder content on the reactivity of CPB containing superplasticizer										
CPB – 0.125- 3%PCI	3.0	100	0	0	ST	7.35	0.125	15	20	7, 28, 60, 90
CPB – 4.5%PCI	4.5	100	0	0	ST	7.35	0.125	15	20	7, 28, 60, 90
CPB – 6.0%PCI	6.0	100	0	0	ST	7.35	0.125	15	20	7, 28, 60, 90

6.2.4. Microstructural analyses

In addition to the OC test, some microstructural analyses tests were conducted on selected samples to have a better understanding on the reasons behind the observed behaviours. These tests include thermogravimetric and differential thermogravimetric (TG&DTG) analysis; X-ray powder diffraction (XRPD); and mercury intrusion porosimetry. For the TG&DTG and XRPD tests, dried powder of cement paste samples (W/C ratio = 1) with admixture and pyrite contents similar to those of the samples being analysed were used. However, CPB samples identical to samples tested for reactivity were used for the MIP test. Before any microstructural analysis, the samples were oven-dried at 45^{o}C temperature for at least four days. The TG&DTG analysis was carried out at the University of Ottawa Advanced Research Complex using a thermogravimetric analyzer Q5000 TGA (TA Instruments, USA). Specimens were heated from room temperature to 1000 ^{o}C at a heating ramp of 10 ^{o}C per minute in a Nitrogen atmosphere. The XRPD analysis was also conducted at the University of Ottawa using a Rigaku ultima IV diffractometer (Rigaku, Japan) operated with a scan voltage of 40 kV, current of 30 mA, and a scan rate of 1 degree per minute. The MIP was conducted at the energy systems design laboratory of the University of Alberta using Quantachrome PoreMaster 33 (Quantachrome Instruments, USA).

6.2.5 Monitoring of electrical conductivity

One of the suitable means of assessing the progression of chemical reaction in the CPB is through the electrical conductivity (EC) test. A 5TE sensor (by Meter Group Inc., USA) was used to monitor the EC from the time of casting up to 60 days of curing. The sensor can measure EC values from 0 to 23 dS/m with an accuracy of ±10%.

6.3 Results and discussions

6.3.1 Time-dependent evolution of the reactivity of CPB containing superplasticizer

The evolution of the reactivity of CPB containing different dosages of PCSP and made with ST and NT is shown in Figures 6.3 and 6.4 respectively. A pyrite content of 15% was added in each sample. In each case, it can be observed that the reactivity of the CPB decreases as time passes. The highest drop in reactivity occurs from 3 to 7 days in curing, after which the change became relatively uniform. For example, the reactivity CPB sample containing 0% PCSP dropped from 0.37 moles O_2/m^2/day to 0.32 moles O_2/m^2/day (~3.5% decrease per day) between day 3 and day 7. However, the daily change is only about 1.6% and 0.6% for the 7-28 days period and 28-60 days interval respectively. The time-dependent change in the CPB reactivity is due to transformations as a result of binder hydration. Certain factors, such as degree of saturation, the porosity of the CPB, the amount of coating surrounding the sulphidic minerals by other compounds, and the exposed surface area have been found to influence the reactivity of CPB (Ouellet et al., 2006; Aldhafeeri and Fall, 2016). The first three factors can all be regulated by the binder hydration in the CPB, whereby clinker compounds (e.g., silicates, aluminates, and oxides) react with water to generate a range of hydration products. As a result, the porewater in the CPB is used off (Taylor, 1997; Thomas et al., 2001) and the new products fill up the pores in the CPB (Ghirian and Fall, 2014) as well as cover some reactive minerals (Ouellet et al., 2006). It can be observed from the evolution of EC (Figure 6.5) that there is a high chemical activity in the CPB in the initial curing time after casting with a peak of 4.3 dS/cm after about 7 hours for the CPB containing 0% PCSP. Likewise, the EC reached a peak of 4.34 dS/cm after about 33 hours for the CPB containing 0.125% PCSP. The activity or hydration of the binder is accompanied by the consumption of the pore water in the CPB. This supports the assertion that the pore water in the

CPB (which is important for the oxidation of sulphide minerals) is consumed by the binder hydration. Furthermore, the TG&DTG graphs presented in Figure 6.6 indicate that there is a difference in the amount of hydration products present in 7-day and 28-day cured specimens. The three peaks in the graphs represent the decompositions of different categories of hydration products. The spike found within the temperature range of 100 ^{o}C to 200 ^{o}C is caused by the dehydration of ettringite, carboaluminates, calcium silicate hydroxide (CSH), and gypsum. The second spike occurring in the temperature range of 450 ^{o}C to 600 ^{o}C is mainly due to the decomposition of calcium hydroxide (CH). The final peak within the temperature range of 650 ^{o}C to 750 ^{o}C is due to the decomposition of calcites and carbonates. In all the three phases of huge mass loss, the 28-day specimen exhibited higher peaks than the 7-days sample. This signifies that the amount of hydration products (especially CH, which has a wider gap), in the CPB increases significantly as the curing time increased. Consequently, the CPB becomes more stable as the reactive minerals are neutralised.

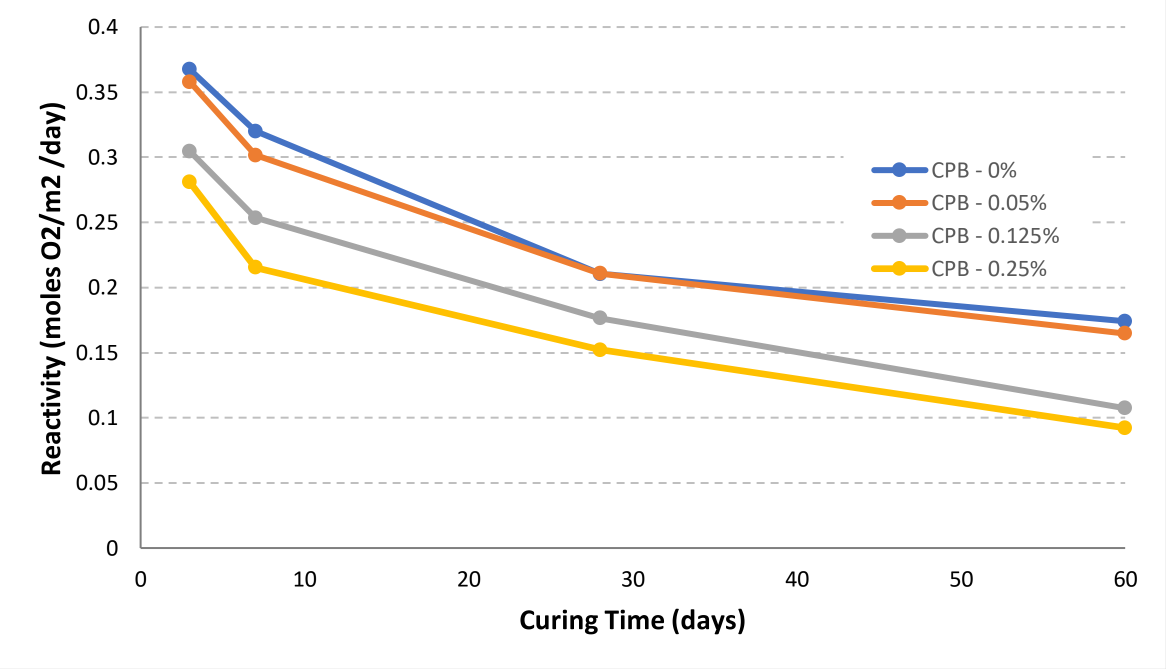


Figure 6.4. Reactivity of ST-CPB containing different dosages of PCSP

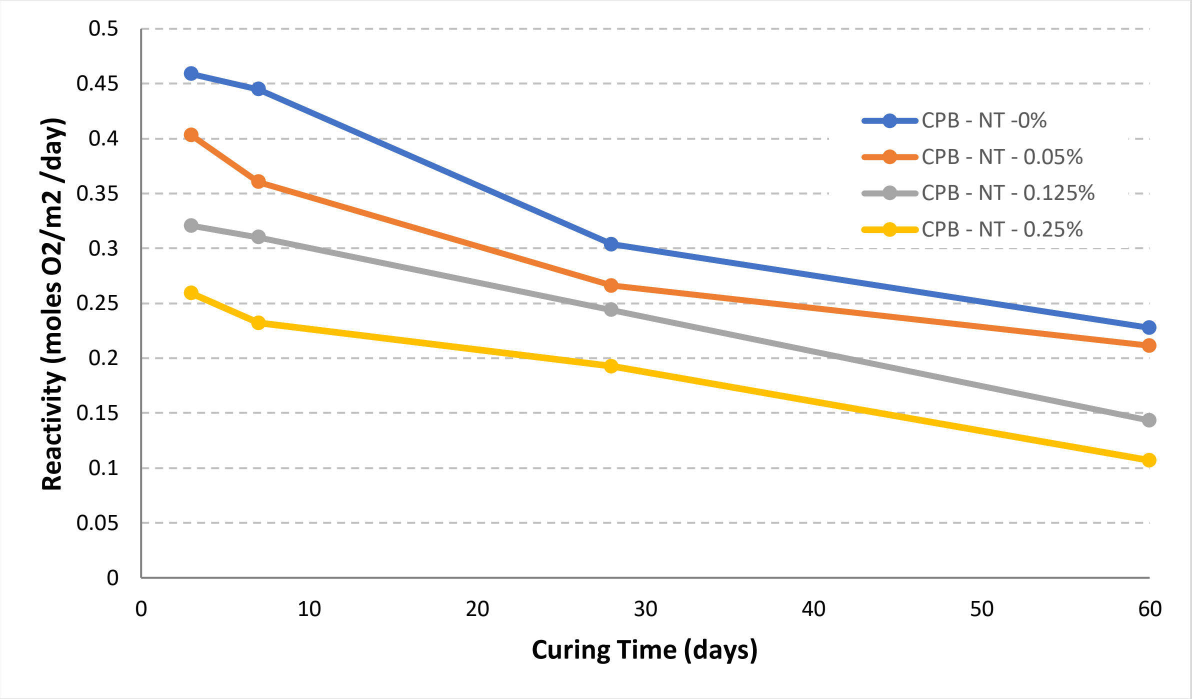


Figure 6.5. Reactivity of NT-CPB containing different dosages of PCSP

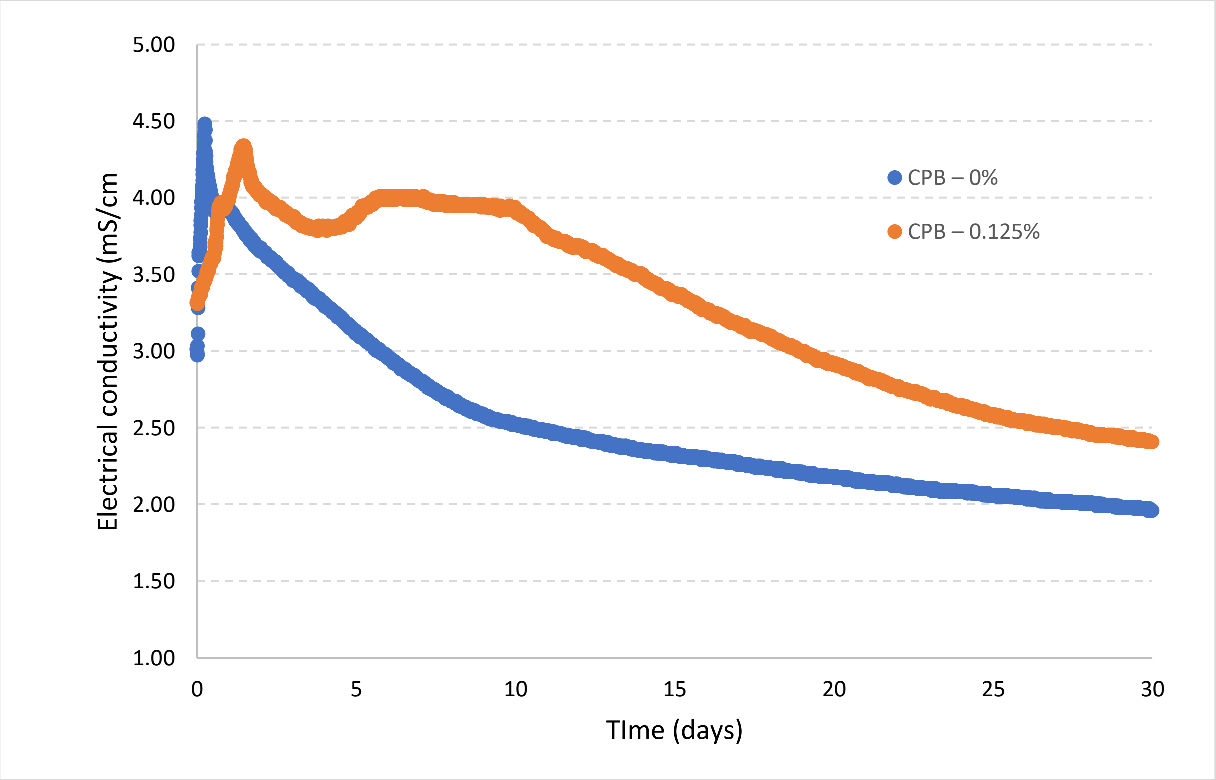


Figure 6.6. Evolution of electrical conductivity in the CPB containing 15% pyrite

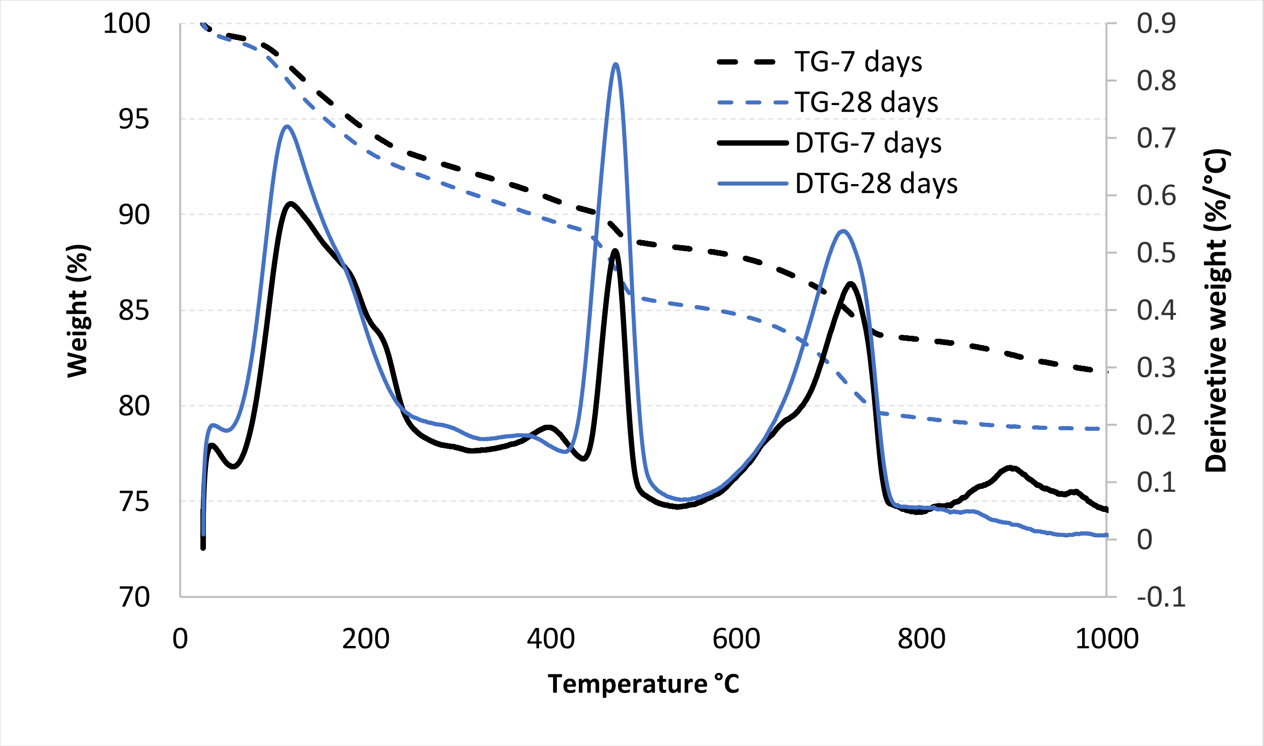
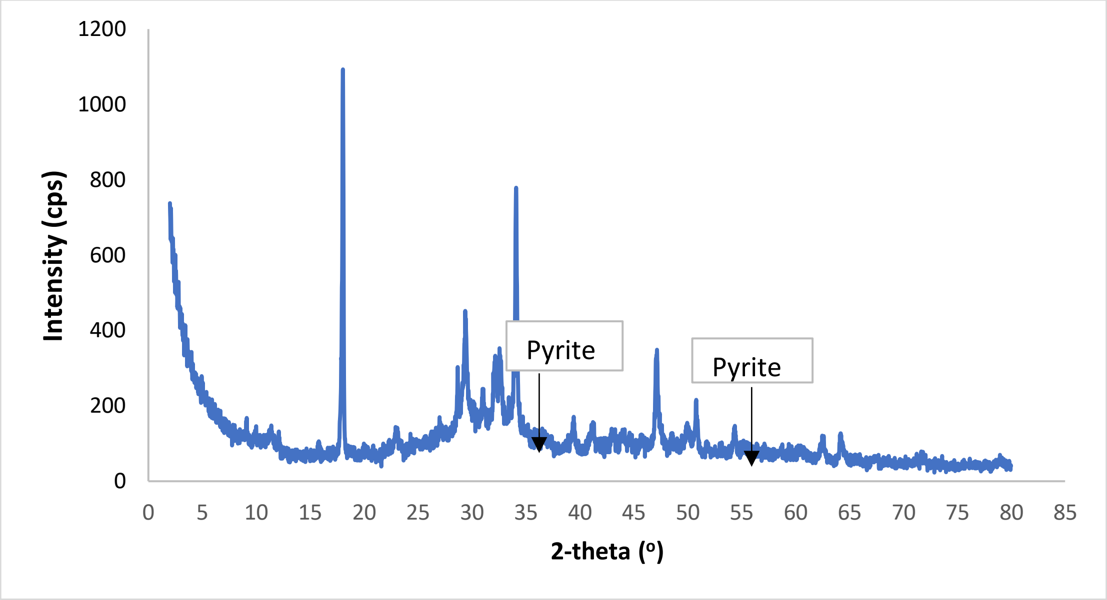
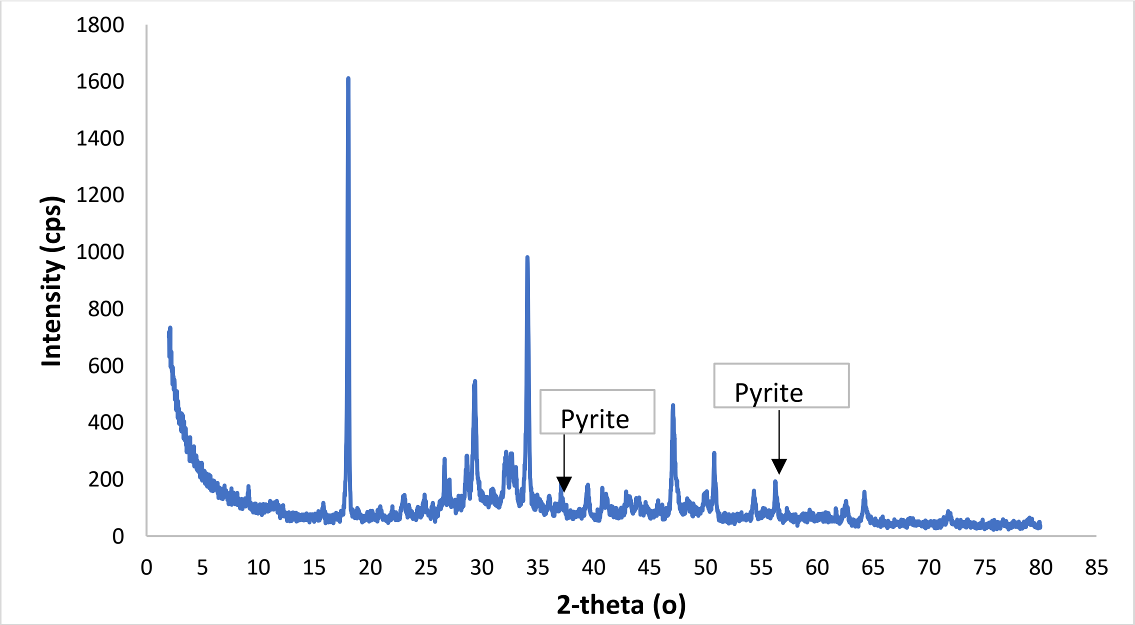


Figure 6.7. TG/DTG diagrams for cement paste with different curing periods

The addition of PCSP in the CPB also shows an inverse effect on the reactivity for both ST and NT. At 3 days curing of ST-CPB, the addition of 0.125% and 0.25% PCSP reduces the reactivity by 17% and 23%, respectively. At 60 days, the respective reductions are 38% and 47% in comparison with the reactivity of CPB containing 0% PCSP. This shows that the use of a PCSP is beneficial in mitigating AMD generation by CPB structures. There are at least three ways in which the superplasticizer could influence the reactivity: i) Interaction with the sulphidic minerals to generate less or non-reactive compounds, ii) change of the binder hydration kinetics, and iii) improvement of the CPB pore structure through self-consolidation. Previous studies have shown that PCP has a tendency of reacting with various compounds in cementitious materials to generate new organo-mineral products (Plank et al., 2010; Habbaba et al., 2014; Pan et al., 2016). In an experimental study by Leemann et al. (2010), naphthalene-sulphonate-based and polycarboxylate-based superplasticizers were observed to increase the alkali-silica reaction in both concrete and mortar. The alkali metals (mostly Na and K) contained in the superplasticizers react with the silicates in the cement to produce varying amounts of hydroxides. He et al. (2020) also observed that sulphate ions within cement paste compete with cement particles in PCSP adsorption. These changes would undoubtedly affect the amount of sulphide minerals available for AMD reaction when exposed to the atmosphere. It can be observed from Figure 6.7 that there is higher amount of pyrite left in the specimen containing 0% PCSP than the specimen containing 0.125% PCSP. The pyrite peaks in the specimen containing 0% PCSP have intensities of about 200 cps and 180 cps, while the peaks are less than 50 cps each for the specimen containing 0.125% PCSP. This is likely due to the transformation of some pyrite into other non-reactive minerals. As for the influence of the PCSP on binder hydration, it is a well known fact that superplasticizers such as PCSP cause retardation of cement hydration during the first few hours of mixing but improve it at later curing ages (Singh et al., 1992; He et al., 2017; Haruna and Fall, 2021). The slow hydration in the immediate time of mixing is a result of the adsorption of the PCSP on the cement particles (Zhang et al., 2014). As it can be observed from the evolution of EC in the CPB containing 0% and 0.125% PCSP (Figure 6.5), even though the peak of the ionic activity is recorded late (retardation), the EC remains higher in the specimen containing superplasticizer from about 1 day of curing. Kong et al. (2016) observed a similar variation in the generation of hydration heat in cement paste containing various contents of PCSP. Finally, the incorporation of superplasticizer has also been associated with refinement of the CPB pore structure as a result of self-consolidation of the solid particles (Arezoumandi and Volz, 2014; Ouattara et al., 2017). The MIP graphs (Figure 8) show that 0.125% PCSP sample has less total porosity than the 0%. As mentioned earlier, the reactivity of sulphate bearing tailings is influenced by the exposed surface area and the pore structure. As the CPB becomes denser, less surface area would be available for the oxidation of pyrite when exposed to the atmosphere. Also, less porosity means that oxygen diffusion within the CPB will be limited, which signifies less reactivity.



a)



b)

Figure 6.8. XRD diagrams for 7-day samples containing a) 0% PCSP and b) 1.25% PCSP

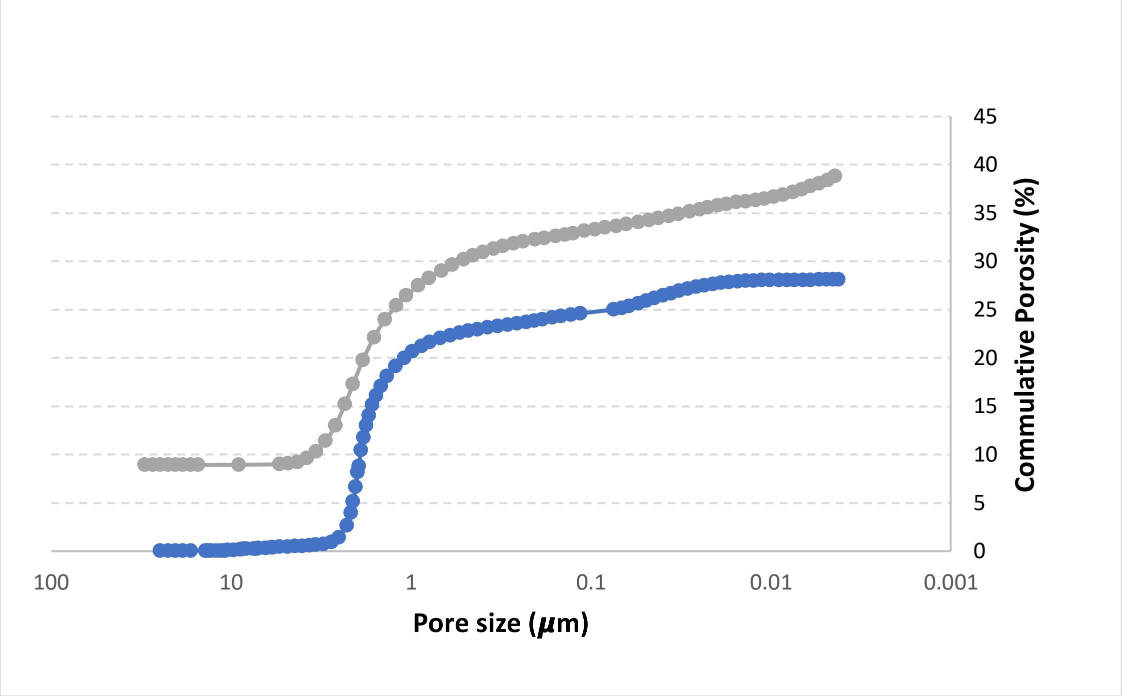


Figure 6.9. Total porosity for CPB containing different superplasticizer contents

5.3.2 Effect of temperature on the reactivity of CPB containing superplasticizer

The evolution of reactivity of CPB samples with 0.125% PCSP and 15% pyrite content, cured at ambient temperatures of 2 °C, 20 °C and 35 °C is presented in Figure 6.9. The results show that curing temperature has an inverse relationship with the reactivity regardless of the curing age. Decreasing the temperature from the room (20 °C) to 2 °C results in the increase of reactivity by 31% and 100% at 3 days and 60 days of curing. Increasing the temperature from room to 35 °C reduces the reactivity by 21% and 53% at the same curing periods. The behaviour can largely be attributed to the increase of cement hydration degree induced by temperature increase. Generation of more hydration products (e.g., ettringite, gypsum, CH, and CSH) results in the refinement the pore structure of the CPB mass (Lamond and Pielert, 2006; Fall and Samb, 2009;), which in turn reduces the rate of oxygen diffusion in the material. Moreover, improved cement hydration produces a more hardened CPB with less loose reactive compounds (Bertrand, 1998; Cihangir et al., 2012). The TG&DTG diagrams presented in Figure 6.10 clearly show the difference in the hydration products in cement pastes cured at different temperatures. The remaining specimen mass at the end of the heating period (1000 ºC) is about 75% for the 20 ºC specimen and 73% for the 35 ºC specimen. This affirms that more hydration products decomposed during the thermal analysis represented by the higher peaks in the DTG curve. The evidence for the pore structure refinement by the increased hydration products at higher temperatures can be seen in the MIP graphs presented in Figure 6.11. The 35 ºC sample has 25% less porosity as compared to the 20 ºC sample. Also, the incremental porosity shows that the pores in the 35 ºC sample are mostly finer that the pores in the 20 ºC sample.

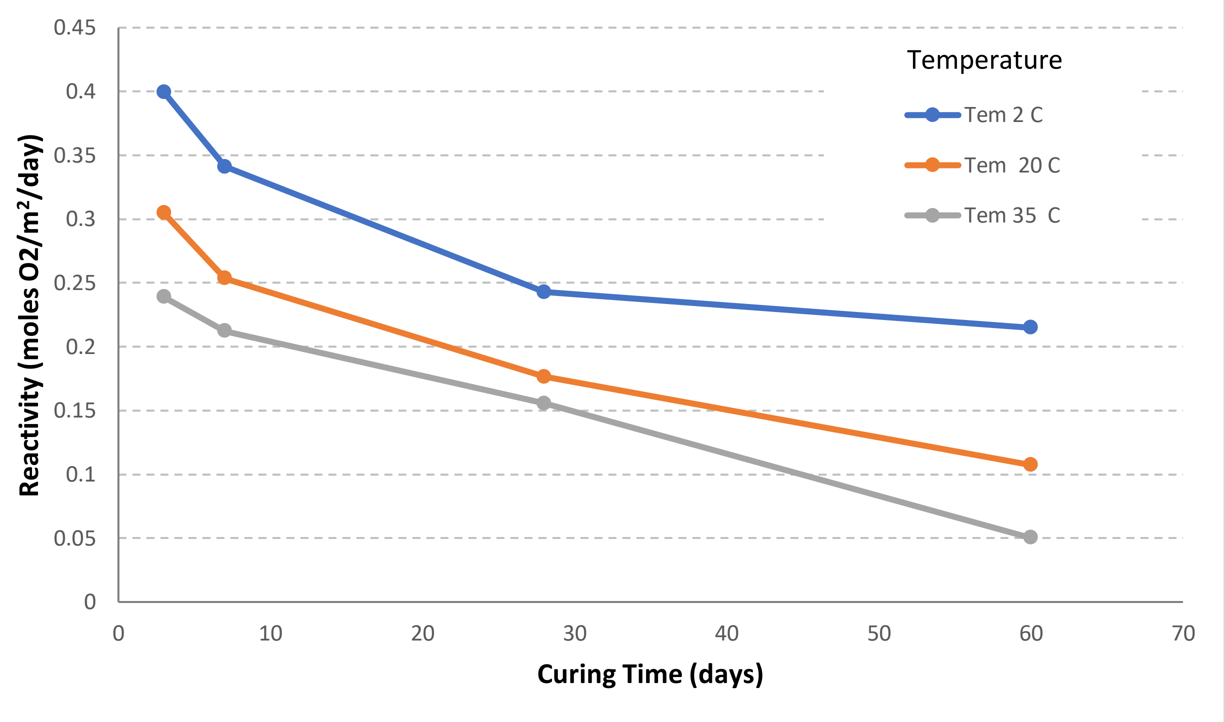


Figure 6.10. Reactivity of ST-CPB containing 0.125% PCSP and 15% Pyrite with different curing temperatures

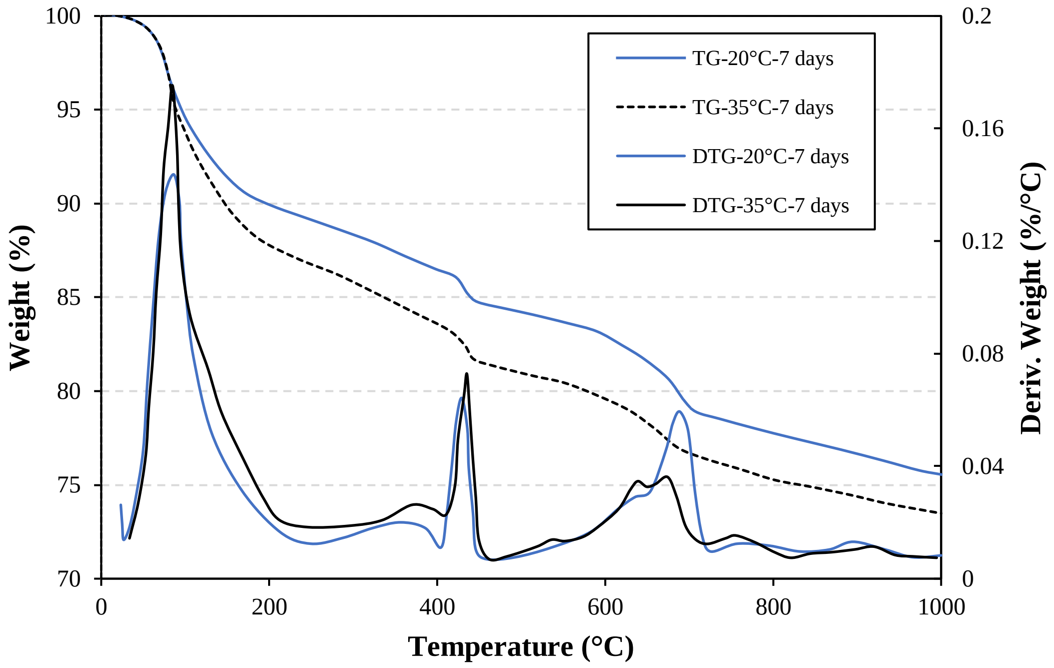


Figure 6.11. TG&DTG diagrams for cement paste cured at 20 ^{o}C and 35 ^{o}C

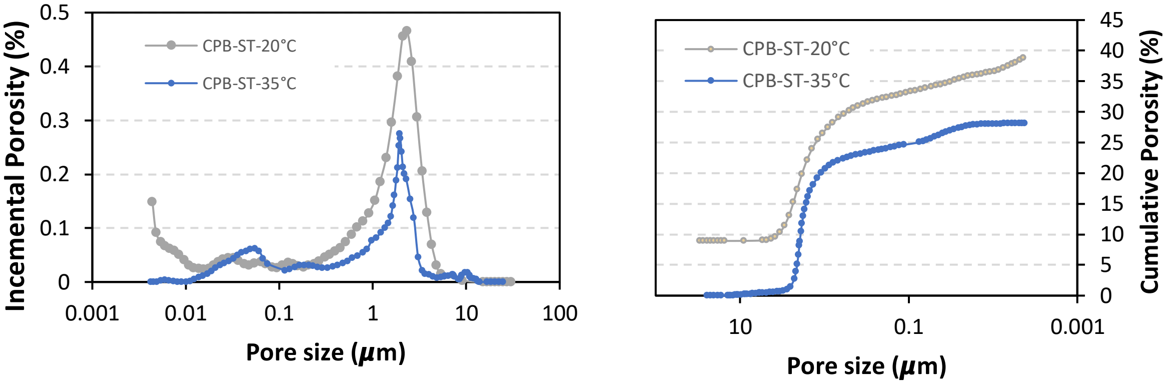


Figure 6.12. Incremental and cumulative porosity of CPB samples cured at 20 ^{o}C and 35 ^{o}C

6.3.3 Effect of binder type on the reactivity of CPB containing superplasticizer

Replacement of PCI with 50% of Slag and FA is also observed to affect the reactivity of the CPB containing PCSP (Figure 6.12). The PCI/FA exhibited the least reactivity throughout the curing period. The PCI/Slag specimens show lower reactivity than the PCI specimens at 3 and 7 days. However, the two have relatively similar reactivity at 28 and 60 days. The reduction of the reactivity as a result of partial replacement of PCI with FA or Slag is largely due to the filler effect of the two pozzolans (Wang and Le, 2010; Aldhafeeri and Fall, 2017). As presented in Table 6.2, the surface areas of FA (2,200 cm^2/g) and Slag (2,100 cm^2/g) are much greater than the surface area of PCI (1,300 cm^2/g). Large surface area translates to smaller particle size, making the pozzolans effective micro-fillers in the CPB. This claim is supported by the MIP results shown in Figure 6.13, for which the total porosity in the PCI specimen is significantly higher than the PCI/FA and PCI/slag. As stated earlier, more porous CPB permits higher diffusion of oxygen, which results in higher magnitude of pyrite oxidation. Besides their smaller size, FA particles are also more spherical than both PCI and Slag, which enhances its filler effects (Mehta, 2004). It is important to note that, the CPB containing 100 PCI will produce the highest amount of hydration product in the long run, which makes the difference in reactivity at 60 days much lower. For instance, the reactivity of the PCI/FA CPB is about 30% less than that of the PCI CPB after 3 days of curing. However, the difference is only about 12% after 60 days curing.

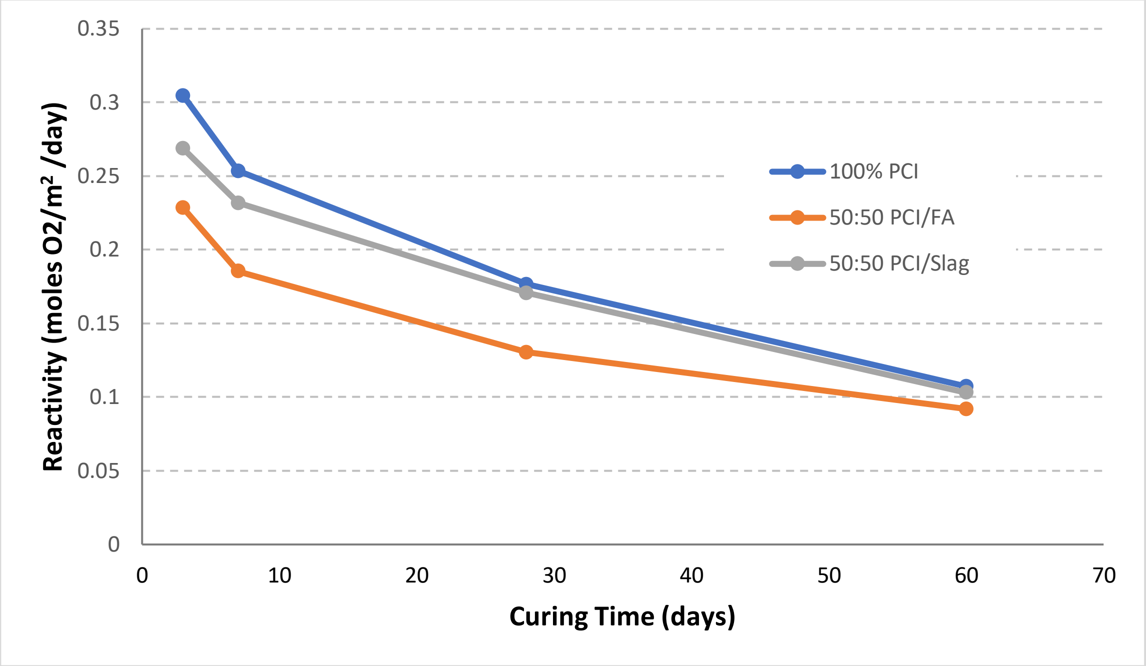


Figure 6.13. Reactivity of CPB containing 0.125% PCSP and 15% pyrite made with various binder types

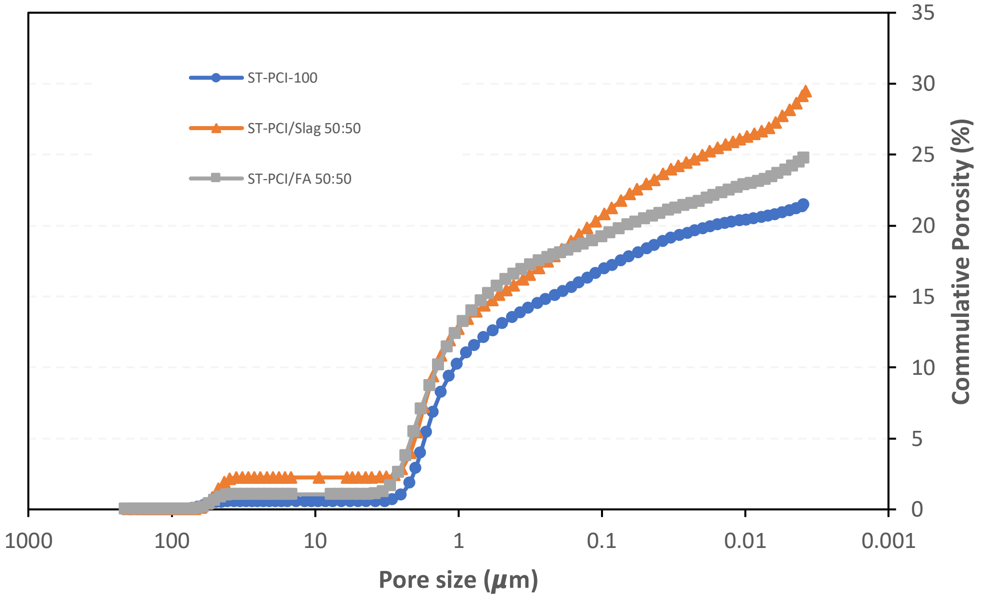


Figure 6.14. MIP results for 7-days CPB samples containing different binder types

6.3.4 Effect binder proportion on the reactivity of CPB

As presented in Figure 6.14, the amount of PCI in the CPB containing superplasticizer also affects the pyrite reactivity. The results show that increasing the percentage of binder in the CPB results the decrease of reactivity. The primary reason for that is the generation of more hydration product as the PCI content increases, which in turn decreases the porosity of the CPB (Fall et al., 2010; Godbout et al., 2007). With more refined pore structure, less oxygen diffuses into the CPB mass, thereby lowering the reactivity. Aldhafeeri and Fall (2017) had a similar observation on a CPB made without any water-reducing admixtures. Thus, the addition of PCSP does not hinder the improvement caused by increasing the cement content in the CPB mixture.

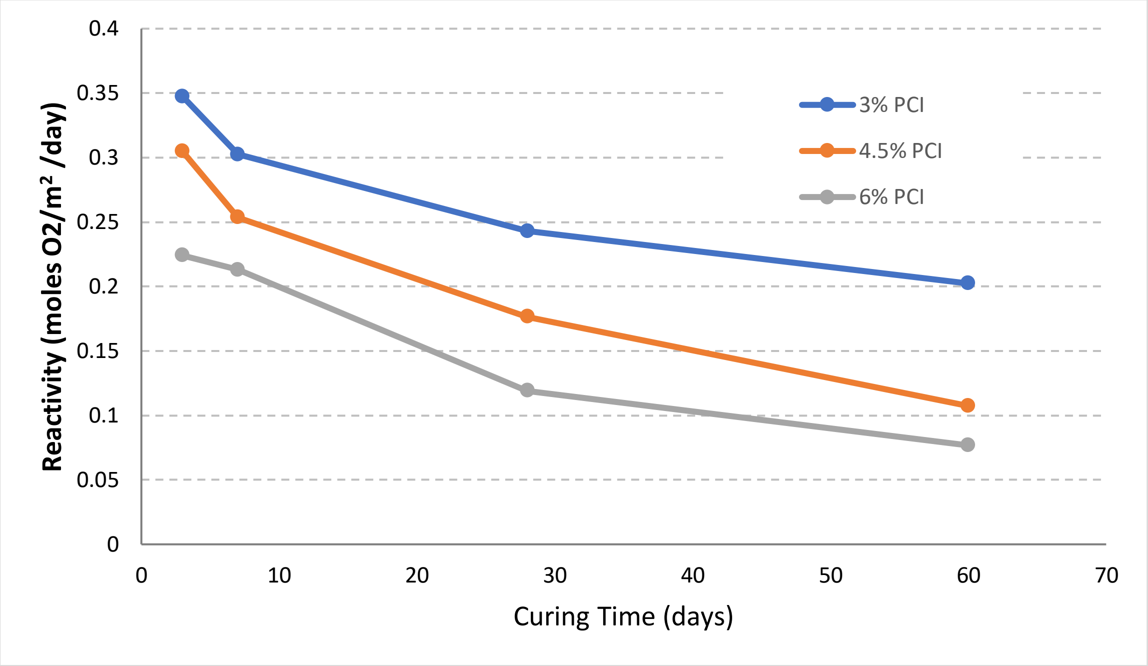


Figure 6.15. Reactivity of ST-CPB containing 0.125% PCSP and 15% Pyrite with different binder contents

6.4 Summary and conclusions

The effects of polycarboxylate-based superplasticizer and other factors on the reactivity of cemented paste backfill containing pyrite (Fe_2S_2) was experimentally investigated using oxygen consumption test. Based on the results obtained and the explorative evidence from various microstructural analyses, the following conclusions are drawn.

1. The reactivity of the CPB decreases proportionately with the increase in the proportion of the superplasticizer in the mixture. Even though the initial pyrite content was the same, the CPB containing superplasticizer had lower pyrite content after curing, which indicates a potential interaction between the two compounds. Besides this, the reduction is also associated with a long-term improvement of binder hydration and self-consolidation caused by the superplasticizer. Both factors reduce the porosity of the CPB that is needed for oxygen diffusion.
2. Ambient curing temperature has a significant influence on the reactivity of CPB containing polycarboxylate superplasticiser. As the temperature is increased, more hydration products are generated, which reduce the porosity in the CPB.
3. Partial replacement of the FA and Slag in the CPB also reduces the reactivity. Both pozzolans act as micro-fillers owing to their large surface areas as compared to Portland cement.
4. Increasing the binder content also reduces the reactivity of CPB. The improvement is linked to the reduction of the porosity in the CPB due to an increase of hydration products.

6.5 References

Aldhafeeri, Z., & Fall, M. (2016). Time and damage induced changes in the chemical reactivity of cemented paste backfill. *Journal of Environmental Chemical Engineering*, *4*(4), 4038-4049.

Aldhafeeri, Z., & Fall, M. (2017). Sulphate induced changes in the reactivity of cemented tailings backfill. *International Journal of Mineral Processing*, *166*, 13-23.

Akcil, A., & Koldas, S. (2006). Acid Mine Drainage (AMD): causes, treatment and case studies. Journal of cleaner production, 14(12-13), 1139-1145.

Arezoumandi, M., & Volz, J. S. (2014). Shear strength of chemically based self-consolidating concrete beams: fracture mechanics approach versus modified compression field theory. *Journal of materials in civil engineering*, *26*(4), 713-720.

ASTM. Standard C494/C494M (2015). *Standard Specification for Chemical Admixtures for Concrete. ASTM International, West Conshohocken, PA*, *29*.

Barabanshchikov, Y. G., & Komarinskiy, M. V. (2014). Influence of superplasticizer S-3 on the technological properties of concrete mixtures. In *Advanced Materials Research* (Vol. 941, pp. 780-785). Trans Tech Publications Ltd.

Belem, T., & Benzaazoua, M. (2008). Design and application of underground mine paste backfill technology. Geotechnical and Geological Engineering, 26(2), 147-174.

Benzaazoua, M., Marion, P., Picquet, I., & Bussière, B. (2004). The use of pastefill as a solidification and stabilization process for the control of acid mine drainage. *Minerals engineering*, *17*(2), 233-243.

Bertrand, V. J. (1998). A study of pyrite reactivity and the chemical stability of cemented paste backfill (Doctoral dissertation, University of British Columbia).

Bravo, M., De Brito, J., Evangelista, L., & Pacheco, J. (2017). Superplasticizer's efficiency on the mechanical properties of recycled aggregates concrete: Influence of recycled aggregates composition and incorporation ratio. *Construction and Building Materials*, *153*, 129-138.

Cihangir, F., Ercikdi, B., Kesimal, A., Turan, A., & Deveci, H. (2012). Utilisation of alkali activated blast furnace slag in paste backfill of high-sulphide mill tailings: effect of binder type and dosage. *Minerals Engineering*, *30*, 33-43.

De Andrade Lima, L. R. P., Bernardez, L. A., & Barbosa, L. A. D. (2008). Characterization and treatment of artisanal gold mine tailings. Journal of Hazardous Materials, 150(3), 747-753.

Dold, B. (2014). Evolution of acid mine drainage formation in sulphidic mine tailings. Minerals, 4(3), 621 641.

Edraki, M., Baumgartl, T., Manlapig, E., Bradshaw, D., Franks, D. M., & Moran, C. J. (2014). Designing mine tailings for better environmental, social and economic outcomes: a review of alternative approaches. Journal of Cleaner Production, 84, 411-420.

Elberling, B., Schippers, A., & Sand, W. (2000). Bacterial and chemical oxidation of pyritic mine tailings at low temperatures. *Journal of contaminant hydrology*, *41*(3-4), 225-238.

Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine tailings. *Water Resources Research*, *32*(6), 1773-1784.

Fall, M., Benzaazoua, M., & Saa, E. G. (2008). Mix proportioning of underground cemented tailings backfill. Tunnelling and Underground space technology, 23(1), 80-90.

Fall, M., & Samb, S. S. (2009). Effect of high temperature on strength and microstructural properties of cemented paste backfill. *Fire Safety Journal*, *44*(4), 642-651.

Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, *114*(3-4), 397-413.

Gelardi, G., & Flatt, R. J. (2016). Working mechanisms of water reducers and superplasticizers. In *Science and technology of concrete admixtures* (pp. 257-278). Woodhead publishing.

Ghirian, A., & Fall, M. (2014). Coupled thermo-hydro-mechanical–chemical behaviour of cemented paste backfill in column experiments: Part II: Mechanical, chemical and microstructural processes and characteristics. *Engineering Geology*, *170*, 11-23.

Godbout, J., Bussière, B., & Belem, T. (2007). Evolution of cemented paste backfill saturated hydraulic conductivity at early curing time.

Griesser, A. (2002). *Cement-superplasticizer interactions at ambient temperatures* (Doctoral dissertation, Swiss Federal Institute of Technology Zurich).

Gui, M. M., Fang, Y. H., Lan, Z. D., Yu, F. Y., Lin, T. X., Jiang, Z. J., & Wen, Q. R. (2011). The compounding and application mechanism of polycarboxylate-based superplasticizers in the self-compacting concrete. In *Advanced Materials Research* (Vol. 250, pp. 711-717). Trans Tech Publications Ltd.

Habbaba, A., Dai, Z., & Plank, J. (2014). Formation of organo-mineral phases at early addition of superplasticizers: The role of alkali sulfates and C3A content. *Cement and concrete research*, *59*, 112-117.

Haruna, S., & Fall, M. (2021). Strength development of cemented tailings materials containing polycarboxylate ether-based superplasticizer: Experimental results on the effect of time and temperature. *Canadian Journal of Civil Engineering*, *48*(4), 429-442.

He, Y., Zhang, X., & Hooton, R. D. (2017). Effects of organosilane-modified polycarboxylate superplasticizer on the fluidity and hydration properties of cement paste. *Construction and Building Materials*, *132*, 112-123.

Ilg, M., & Plank, J. (2019). Synthesis and properties of a polycarboxylate superplasticizer with a jellyfish-like structure comprising hyperbranched polyglycerols. *Industrial & Engineering Chemistry Research*, *58*(29), 12913-12926.

Jennings, S. R., Blicker, P. S., & Neuman, D. R. (2008). Acid mine drainage and effects on fish health and ecology: a review. Reclamation Research Group.

Kong, F. R., Pan, L. S., Wang, C. M., & Xu, N. (2016). Effects of polycarboxylate superplasticizers with different molecular structure on the hydration behavior of cement paste. *Construction and building materials*, *105*, 545-553.

Kossoff, D., Dubbin, W. E., Alfredsson, M., Edwards, S. J., Macklin, M. G., & Hudson Edwards, K. A. (2014). Mine tailings dams: characteristics, failure, environmental impacts, and remediation. Applied Geochemistry, 51, 229-245.

Lamond, J. F., & Pielert, J. H. (2006). *Significance of tests and properties of concrete and concrete-making materials* (Vol. 169). ASTM international.

Landriault, D. (2001). Backfill in underground mining. *Underground mining methods: engineering fundamentals and international case studies*, 601-614.

Leemann, A., Lothenbach, B., & Thalmann, C. (2011). Influence of superplasticizers on pore solution composition and on expansion of concrete due to alkali-silica reaction. *Construction and building materials*, *25*(1), 344-350.

Li, Y. (2021). Comprehensive Benefit Evaluation of Cemented Paste Backfill in the Mining Industry. Advances in Civil Engineering, 2021.

Lottermoser, B. G. (2010). Tailings. In Mine wastes (pp. 205-241). Springer, Berlin, Heidelberg.

Liao, Tung-Sheng, Chao-Lung Hwang, Yi-Shian Ye, and Kung-Chung Hsu. "Effects of a carboxylic acid/sulfonic acid copolymer on the material properties of cementitious materials." *Cement and Concrete Research* 36, no. 4 (2006): 650-655.

Marchon, D., & Flatt, R. J. (2016). Impact of chemical admixtures on cement hydration. In *Science and technology of concrete admixtures* (pp. 279-304). Woodhead Publishing.

Mehta, P. K. (2004, May). High-performance, high-volume fly ash concrete for sustainable development. In *Proceedings of the international workshop on sustainable development and concrete technology* (pp. 3-14). Ames, IA, USA: Iowa State University.

Mohapatra, D. P., & Kirpalani, D. M. (2017). Process effluents and mine tailings: sources, effects and management and role of nanotechnology. Nanotechnology for Environmental Engineering, 2(1), 1-12.

Ouattara, D., Yahia, A., Mbonimpa, M., & Belem, T. (2017). Effects of superplasticizer on rheological properties of cemented paste backfills. International Journal of Mineral Processing, 161, 28-40.

Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. Minerals engineering, 19(5), 407-419.

Pan, Y. F., Jiang, Y. Q., & Zhang, S. J. (2016). Study on the effect of condensate-type and copolymer-type combined superplasticizers on hydration of cement. In *Key Engineering Materials* (Vol. 703, pp. 360-364). Trans Tech Publications Ltd.

Pei, M., Wang, Z., Li, W., Zhang, J., Pan, Q., & Qin, X. (2008). The properties of

Cementitious materials superplasticized with two superplasticizers based on aminosulfonate–phenol–formaldehyde. *Construction and Building Materials*, *22*(12), 2382-2385.

Pereira, P., Evangelista, L., & De Brito, J. M. C. L. (2012). The effect of superplasticisers on the workability and compressive strength of concrete made with fine recycled concrete aggregates. *Construction and Building Materials*, *28*(1), 722-729.

Plank, J., Zhimin, D., Keller, H., Hössle, F. V., & Seidl, W. (2010). Fundamental mechanisms for polycarboxylate intercalation into C3A hydrate phases and the role of sulfate present in cement. Cement and concrete research, 40(1), 45-57.

Poole, J. L., Riding, K. A., Juenger, M. C., Folliard, K. J., & Schindler, A. K. (2011). Effect of chemical admixtures on apparent activation energy of cementitious systems. *Journal of materials in civil engineering*, *23*(12), 1654-1661.

Prezzi, M., Monteiro, P. J., & Sposito, G. (1998). Alkali-silica reaction-Part 2: The effect of chemical admixtures. ACI Materials Journal, 95, 3-10.

Sha, S., Wang, M., Shi, C., & Xiao, Y. (2020). Influence of the structures of polycarboxylate superplasticizer on its performance in cement-based materials-A review. *Construction and Building Materials*, *233*, 117257.

Singh, N. B., Sarvahi, R., & Singh, N. P. (1992). Effect of superplasticizers on the hydration of cement. *Cement and Concrete Research*, *22*(5), 725-735.

Tadros, T. (2013). Electrostatic repulsion and colloid stability. *Encyclopedia of Colloid and Interface Science,* 363-363.

Thomas, J. J., FitzGerald, S. A., Neumann, D. A., & Livingston, R. A. (2001). State of water in hydrating tricalcium silicate and portland cement pastes as measured by quasi-elastic neutron scattering. *Journal of the American Ceramic Society*, *84*(8), 1811-1816.

Taylor, H. F. (1997). *Cement chemistry* (Vol. 2, p. 459). London: Thomas Telford.

Wang, X. Y., & Lee, H. S. (2010). Modeling the hydration of concrete incorporating fly ash or slag. *Cement and concrete Research*, *40*(7), 984-996.

Zhang, Y. R., Kong, X. M., Lu, Z. B., Lu, Z. C., & Hou, S. S. (2015). Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes. *Cement and Concrete Research*, *67*, 184-196.

Zingg, A., Winnefeld, F., Holzer, L., Pakusch, J., Becker, S., Figi, R., & Gauckler, L. (2009). Interaction of polycarboxylate-based superplasticizers with cements containing different C3A amounts. *Cement and Concrete Composites*, *31*(3), 153-162.

Chapter 7. Integration and Synthesis of Results

7.1 Introduction

To fully understand the broad impact of polycarboxylate ether-based superplasticizers on the engineering performance of CPB, the results obtained from all four technical papers are combined and discussed in this chapter. Paper one and two studied the rheological and mechanical properties of CPB containing the superplasticizer. Papers three and four investigated environmental properties by using hydraulic conductivity and reactivity as reference indicators. In each case, the effects of additional factors such as tailings type, binder content, binder type, temperature, curing time, and sulphate content were also studied. The summary of the experimental tests conducted is presented in Table 7.1.

Table 7.1 Different factors studied in the PhD research

Technical Paper	Chapter	Superplasticizer content	Curing time	Tailings type	Binder type	Binder content	Curing Temperature	Effect of W/C ratio	Effect of sulphate content	Coupled THMC processes	Microstructural tests	Monitoring tests
1	3	X	X	X			X				Zeta potential, TG/DTG	EC, Temp, Suction
2	4	X	X	X	X		X			X	TG/DTG, MIP, XRD	EC, Temp, Suction
3	5	X	X	X	X		X	X	X		TG/DTG, XRD, MIP	-
4.	6	X	X	X	X	X	X				TG/DTG, XRD, MIP	EC

EC: Electrical conductivity; Temp.: Temperature; TG/DTG: Thermogravimetry and derivative thermogravimetry; XRD: X-ray diffraction; MIP: Mercury intrusion porosimetry; THMC: Thermal, Hydraulic, Mechanical and Chemical

7.2 Improvement of rheology by the polycarboxylate ether-based superplasticizer

The findings from the series of experimental tests conducted in this study give an insight into the role the superplasticizer being investigated plays on the properties of CPB. The primary purpose of incorporating the admixture is to improve flowability so that the CPB can be easily mixed and transported into the mine stopes with ease. However, this cannot simply be achieved without other properties of the CPB being affected. Therefore, it is important to first describe how the rheology is improved in light of the current research findings.

A simple way of assessing the water-reducing capability of a superplasticizer is by comparing workability using a slump test. The slumps of CPB mixes containing 0% and 0.125% and 0.25% superplasticizer contents are shown in Figure 7.1. A fresh CPB having a binder content of 4.5% and a W/C ratio of 7.6 (typical values used in Canadian mines) has a slump of 22.2 cm. By adding 0.125% and 0.25% polycarboxylate ether-based superplasticizer, the slum values increased to 29.6 cm and 29.8 cm, respectively. Comparatively, an optimum slump for CPB according to Chaoqu et al. (2019) is 24.2 cm. Thus, the improvement by the addition of both proportions of the superplasticizer can be considered to be significant. High slump values for CPB are needed because of the time required to transport the material from the mixing plant on the ground surface to the deep underground mine stopes using pipes.

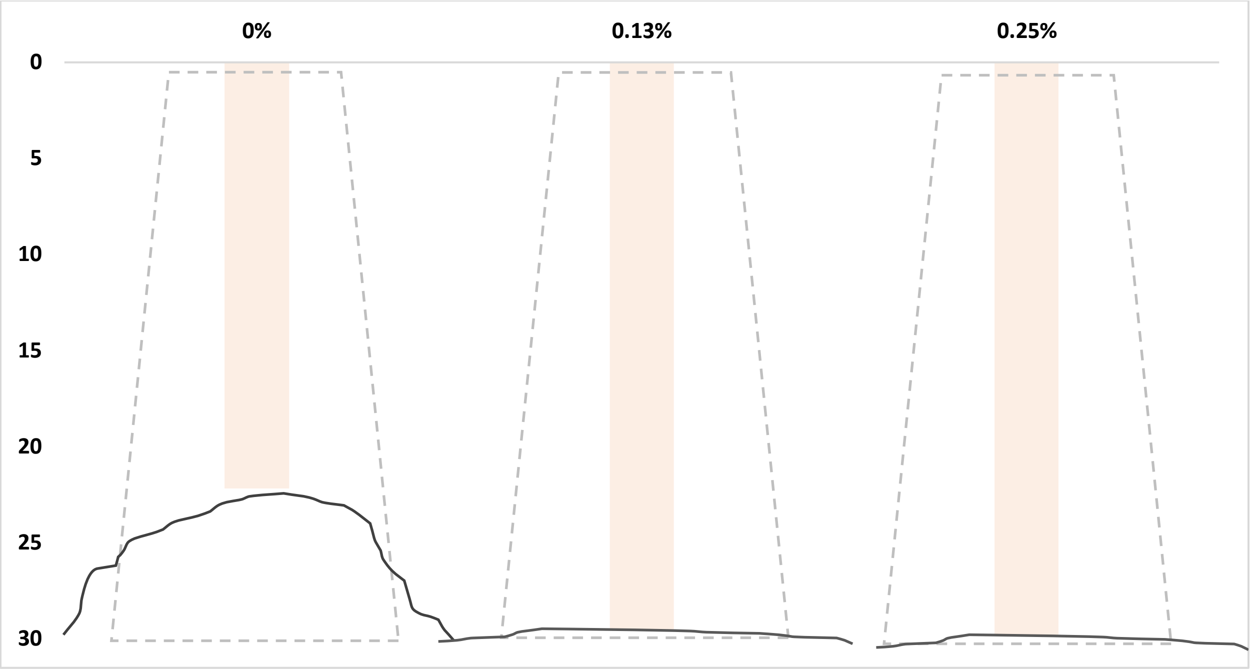


Figure 7.1 Slump of CPB with and without superplasticizer (x-axis: % of PCSP; y-axis: slump value in cm)

When the superplasticizer is added to the CPB, its molecules adsorb themselves on the solid particles, thereby increasing the electrostatic repulsive force. This inhibits the agglomeration of particles in the immediate aftermath of mixing, thus maintaining the fluidity of the CPB. The polycarboxylate ether-based superplasticizer that is used in this study exhibits a uniquely different force through which it improves the rheology of cementitious mixtures, which is called steric hindrance. As the main dispersion mechanism, the steric hindrance prevents the flocculation of solid particles due to the long comb-shape of the poly-oxyethylene molecules in the superplasticizer (Yoshioka et al., 1997). Results from zeta potential and electrical conductivity monitoring support this claim. Fresh CPB samples prepared with 0% and 0.05% superplasticizer contents were observed to have zeta potentials of –3.5 mV and – 10 mV respectively. This means that a stronger repulsive force exists in the presence of the superplasticizer. Also, as there is less contact between the solid particles, the progression of cement hydration becomes affected.

Electrical conductivity monitoring reveals that CPB containing 0% superplasticizer reached the peak of chemical activity about 4 hours after mixing as opposed to 6.7 hours for the CPB containing 0.25% superplasticizer. This means that the CPB containing superplasticizer retains its improved flowability for several hours before it begins thickening (setting) dues to binder hydration.

Besides the curing time, other factors, namely temperature and tailings type were also found to affect the rheology of the CPB. High ambient temperature accelerates the binder hydration, which in turn reduces the flowability of the CPB whether superplasticizer is added or not. The temperature has a negative impact on on both yield stress and viscosity of the CPB. For the tailings types, the variation in the rheology was mainly due to the differences in the physical properties and mineralogical compositions. Denser tailings (with higher specific gravity) and the presence of sulphate are associated with higher yield stress and viscosity. Previous studies have shown that sulphate ions react with calcium hydroxide and tricalcium aluminates to produce gypsum and ettringite, which make the CPB thicker.

7.3 Role of superplasticizer on the Multiphysics processes in CPB

The behaviour of fresh and hardened CPB is regulated by multiple processes in the CPB system, mainly described as thermal, hydraulic, mechanical, and chemical (THMC). It is important to highlight each of the processes as observed from the experimental results of this study.

7.3.1 Thermal process

Temperature changes in CPB arise either i) internally from binder hydration and/or other exothermal reactions such as pyrite oxidation, and ii) externally through heat transfer from the atmosphere or adjacent ground. By monitoring the temperature in the specimens, thermal changes within the CPB samples were observed throughout the curing period. Because the ambient temperature was kept constant using insulated chambers, it is possible to narrow down the source of the temperature change to the chemical reactions in the CPB. With the ambient temperature being constant, the internal temperature generally begins to rise immediately after casting the CPB samples. The heat generation peaked earlier for the samples containing 0% superplasticizer. When a superplasticizer is added, the time to reach the peak increases. With the addition of 0.25% superplasticizer, the increases almost two-fold in comparison with the 0% sample. This observation supports the retardation capability of superplasticizers when added to cementitious materials as observed by other research studies (Lothenbach, 2007; Zhang et al., 2015).

The effects of ambient temperature on the CPB are largely related to how it changes the binder hydration, either by accelerating it or by slowing it down. Based on the microstructural analyses conducted, the amount of hydration products in the CPB is proportional to the curing temperature. For fresh CPB, large quantities of ettringite, gypsum and C-S-H produced at elevated temperature make the CPB thicker, as observed from high viscosity and yield stress values. The temperature effect on the rheology holds whether the superplasticizer is added to the material or not. Thus, a higher percentage of the admixture is needed in the preparation of CPB in hot climates. The properties of hardened CPB, such as its mechanical strength and permeability, are also improved when the degree of hydration increases. This is achieved through the refinement of the pore structure of the CPB structure by the high quantity of hydration products. The more important compound for strength development, calcium silicate hydrate (CSH) gel (Michael, 2019), is also produced in larger quantity at higher ambient temperature.

7.3.2. Hydraulic process

The variations in the hydraulic state of the CPB are significant in backfill design due to the role it plays in the stability of barricades and strength development. Monitoring of volumetric water content (VWC) and negative pore water pressure (matric suction) shows that changes in the CPB saturation are interrelated with other processes. Hydraulic changes in the CPB are also linked to the progression of cement hydration, which consumes the available free water. Because of the retardation effect of the superplasticizer on the cement hydration, the VWC in the CPB remains relatively the same during the initial few hours after mixing. Figures 7.2 and 7.3 present the changes in the VWC and matric suction in the CPB over 28-days. Generally, the hydration process in the CPB progresses rapidly at an early age, which is within the first 14 days in this case. The hydration reaction is accompanied by free water consumption and the production of solid hydrates (hydration products).

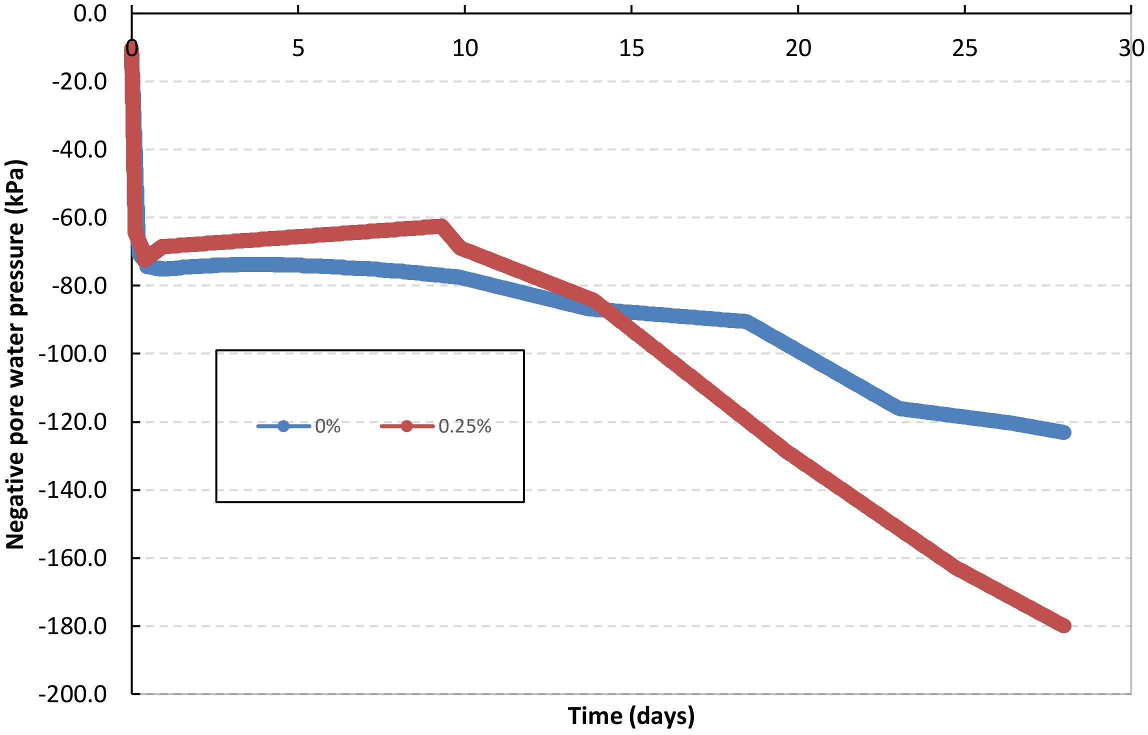


Figure 7.2 Matric suction in the CPB containing different superplasticizer contents

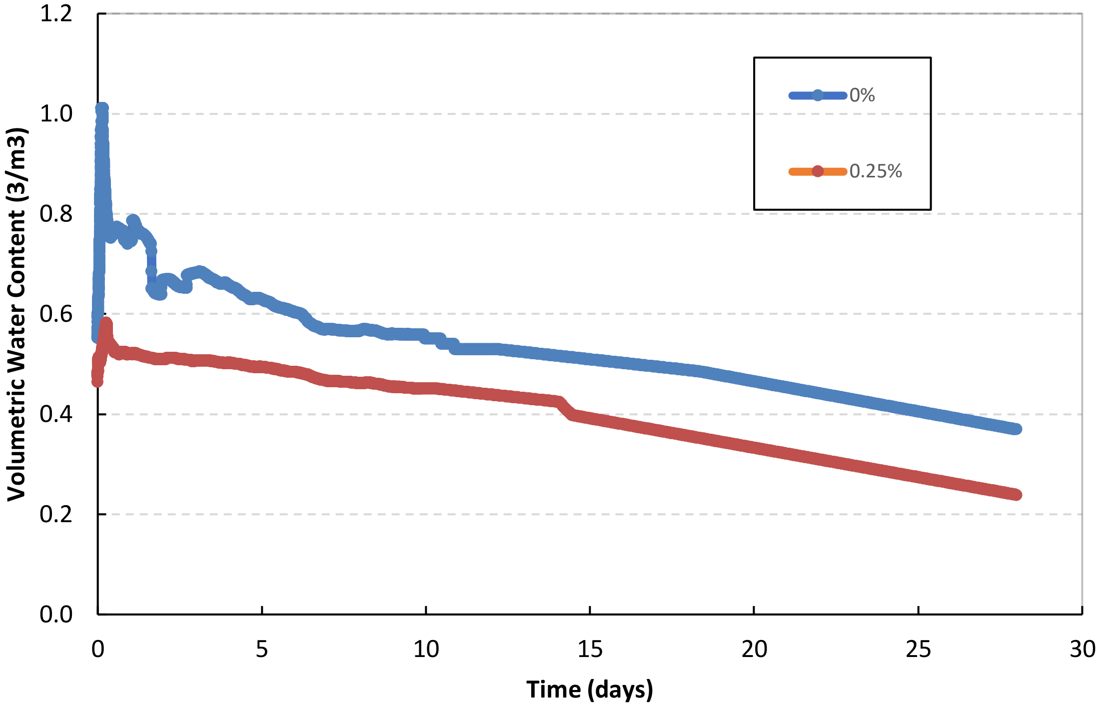


Figure 7.3 Volumetric water content in the CPB containing different superplasticizer contents

The hydraulic state of the CPB also plays an important role in the reactivity of the CPB mass. One of the prerequisites for pyrite oxidation is the presence of water, which provides the hydrogen and oxygen ions for the production of heavy metal and acidic compounds (Lin et al., 2007; Evangelou, 2018). The amount of water in the CPB also affects how much AMD leachate is discharged from the CPB. However, as the free water is used off by the binder hydration, the rate of the CPB reactivity is reduced substantially. The superplasticizer influences these reaction dynamics in different ways. First, the polycarboxylic compound interacts with the sulphide minerals to generate less reactive compounds. It also affects the amount of free water in the CPB at later ages through the enhancement of binder hydration and inducement of self-consolidation.

7.3.3 Mechanical process

The mechanical property of the CPB was measured by the unconfined compressive strength (UCS). It is an important design property that governs the stability of the CPB structure and influences how fast the mining operations can resume after backfilling. The primary factor for the strength development is the binder hydration, which generates byproducts that bind the solid particles together and refine the pore structure in the CPB. At an early age, the strength development in the CPB containing superplasticizer is slower due to the retardation of the hydration process. Beyond 3 days, the superplasticizer significantly enhances the CPB strength. This is achieved by the improvement of the binder hydration at a later age and self-consolidation of the CPB caused by the superplasticizer. Typically, the CPB containing superplasticizer hardens with a finer pore structure.

7.3.4. Chemical process

As discussed in the other sections, most of the changes in the CPB depend on binder hydration, which is the primary chemical process. The degree of hydration at every stage is assessed based on the quantities of the hydration products generated using thermogravimetric analysis. The electrical conductivity (EC) monitoring revealed that hydration reaction typically peaks within the first few hours after mixing, and then continues to decrease with time. The peak is delayed by about twice the time when a superplasticizer content of 0.125% is added to the CPB, although the magnitude of the peak EC value is higher. Thus, the superplasticizer has a retardation effect on the binder hydration but, at the same time, improves the overall magnitude of the binder hydration.

The oxidation reaction is another chemical process in the CPB when sulphide-bearing tailings are used. In such situations, the sulphide compounds (e.g., pyrite) react with oxygen and water to generate heavy metallic and/or acidic compounds. Exposure to the atmosphere is needed to have the required oxygen for the reaction. The rate of the oxidation reaction, which indicates the reactivity of the CPB, is influenced by the superplasticizer as well as the binder hydration. The addition of the polycarboxylate-based superplasticizer appears to reduce the amount of pyrite in the CPB, which is likely due to chemical interaction.

7.4 Environmental performance of CPB containing superplasticizer

Hydraulic conductivity and reactivity of the CPB structures were studied to assess their environmental performance. The reactivity dictates how much toxic compounds are generated from sulphide-bearing CPB when it is exposed to the atmosphere. On the other hand, the hydraulic conductivity governs how the generated compounds are transported into adjacent water bodies. The presence of polycarboxylic-based superplasticizer in the CPB leads to the decrease of both the reactivity and the hydraulic conductivity. The admixture improves the degree of hydration at the later age, which leads to the generation of a large amount of hydration products to fill the CPB pores. Also, the superplasticizer leads to the self-consolidation of the solid particles in the CPB. Both processes are beneficial for the refinement of the CPB pore structure. With less porosity, both the reactivity and hydraulic conductivity are significantly reduced.

7.5 Novel contributions of the research

Although superplasticizers have been used in the construction industries for a long time, their adoption in the preparation of CPB is relatively new. The practical benefits of these admixtures in the production of sufficiently fluid CPB mixture that can effectively be transported underground through several kilometres of pipelines make them indispensable. Besides that, the CPB structures are also required to maintain adequate mechanical stability and be environmentally safe. The existing literature on the use of superplasticizers revealed that polycarboxylic-based types are the most effective in terms of rheological and mechanical strength improvement of the CPB. However, there is a limited understanding of their performance under varying ambient temperature. Also, no studies have been conducted to assess the environmental performance of the CPB containing polycarboxylic-based superplasticizers. This PhD research is aimed at bridging this literature gap. Each technical paper included in this manuscript presents new findings and represents a significant new contribution to CPB technology. The findings will be useful towards the design of economically and environmentally sustainable CPB structures.

7.6 Potential cost savings from the use of superplasticizers

The backfilling process makes up a significant portion of the overall mining operation cost, with some studies estimating it to be up to 20 per cent. Although it is difficult to state the precise savings as a result of the addition of superplasticizer in the preparation of the CPB, there are apparent economic benefits based on the numerous positive effects identified in the study. These include:

1. Elimination or reduction of downtime in the mining process that is often caused by clogging of pipelines used to transport the CPB. Without adequate flowability, fresh CPB may get stuck in the pipes causing all mining operations to halt, with an associated decrease in productivity.
2. Improvement of the compressive strength of the CPB ensures a more stable structure with limited susceptibility to failure. Failure of backfill structures has a huge financial cost implication for the mining industry.
3. Remediation of ground and surface water contamination caused by mining operations has a huge cost implication as well. Improvement of the environmental performance of the CPB ensures that fewer resources are expended on remediation.

7.7 References

Dai, C., Wu, A., Qi, Y., & Chen, Z. (2019). The optimization of mix proportions for cement paste backfill materials via Box–Behnken experimental method. *Journal of The Institution of Engineers (India):* Series D, 100(2), 307-316.

Evangelou, V. B. (2018). *Pyrite oxidation and its control: solution chemistry, surface chemistry, acid mine drainage (AMD), molecular oxidation mechanisms, microbial role, kinetics, control, ameliorates and limitations, microencapsulation*. CRC press.

Harrisson, A. M. (2019). Constitution and Specification of Portland Cement. *Lea's Chemistry of Cement and Concrete*, *5,* 87-155.

Lin, C., Wu, Y., Lu, W., Chen, A., & Liu, Y. (2007). Water chemistry and ecotoxicity of an acid mine drainage-affected stream in subtropical China during a major flood event. *Journal of Hazardous Materials*, *142*(1-2), 199-207.

Lothenbach, B., Winnefeld, F., & Figi, R. (2007). The influence of superplasticizers on the hydration of Portland cement. *Empa, Dübendorf, Switzerland*.

Yoshioka, K., Sakai, E., Daimon, M., & Kitahara, A. (1997). Role of steric hindrance in the performance of superplasticizers for concrete. Journal of the American Ceramic Society, 80(10), 2667-2671.

Zhang, Y. R., Kong, X. M., Lu, Z. B., Lu, Z. C., & Hou, S. S. (2015). Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes. *Cement and Concrete Research*, *67*, 184-196.

Chapter 8. Conclusions and Recommendations

8.1 General conclusions

The use of superplasticizers to improve the flowability of fresh CPB is being widely accepted in the mining industry, therefore understanding their effects under different conditions is essential for an effective design. The following conclusions are drawn based on the results obtained.

1. Addition of superplasticizer to the CPB significantly reduces the yield stress and viscosity of CPB regardless of the tailings type used. An addition of 0.125% of the admixture results in over 50% reduction in yield stress and viscosity at the time of preparation as well as after 4 h. The marginal reduction upon increasing the admixture to 0.25% is much less, indicating that 0.125 is the most effective proportion from the percentages used in the study.
2. Natural tailings exhibit higher yield stress and viscosity than artificial tailings due to their mineralogical compositions and pore water chemistry. This means that, different quantities of superplasticizer are required for different tailings type to achieve the similar flowability improvement. For similar reasons, the hydraulic conductivity and reactivity are both found to be higher in the CPB made with natural tailings.
3. Addition of superplasticizer contents of 0.125% and 0.25% to the CPB results in a significant increase in the UCS as compared to the CPB containing 0%. The improved strength is largely associated with the enhancement of cement hydration by the superplasticizer through ionic diffusion and self-consolidation of solid particles.
4. Partial replacement of the PCI with other binders, namely, fly ash and slag showed a decrease in the compressive strength. However, the decrease is considerably less when

50% of the PCI is replaced with slag as compared to a significant reduction on replacement with fly ash.

5. The curing temperature has a significant influence on both the rheology (viscosity and yield stress) and mechanical strength (UCS) of CPB even when treated with superplasticizer. An increased superplasticizer dosage is required to prepare sufficiently fluid CPB at elevated temperatures. The UCS of the CPB increases by changing the curing temperature in the order of 2 °C > 20 °C > 35 °C. As revealed by the chemical and thermal behaviour of the cement hydration process, the reason lies in the shortening of the onset of the hydration by the superplasticizer when temperature is increased.
6. The polycarboxylate ether-based superplasticizer improves the environmental performance of CPB by reducing both its hydraulic conductivity and reactivity. The reduction is largely due to the influence of the superplasticizer on particles mobility, cement hydration, and interaction with other chemical compounds in the tailings.
7. Increasing the binder content improves the general performance of the CPB, in terms of both mechanical strength and reacivity. The improvement is linked to the reduction of the porosity in the CPB due to an increase of hydration products.

8.2 Recommendations

The following recommendations are made for future work.

1. Other kinds of superplasticizers such as lignosulphates, sulphonated melamines, and sulphonated naphthalenes interact differently from the polycarboxylate-based superplasticizers that was used in this study. Future studies could investigate the effect of each of them on the performance properties of CPB.

2. Further studies on the coupled THMC processes using column experiment or similar large-scale investigation are recommended for understanding near-field beahaviour of CPB containing superplasticizer.
3. The long-term mechanical behaviour of the CPB containing superplasticizer beyond 28 days should be studied.
4. The environmental performance of sulphide-bearing CPB should further be investigated using leachability test in addition to reactivity and hydraulic conductivity.
5. Only three curing temperatures of 2 ^{o}C, 20 ^{o}C, and 35 ^{o}C were used in the study. The effect of freezing and elevated temperatures should be investigated.
6. Further studies are recommended to assess the cost implications and potentials savings from the use of superplasticizers in the preparation of CPB.